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The Working of Metals

FOREWORD

DURING the past twenty-three years, the proceedings or transactions and papers of the Institute of Metals Division have been published in various forms. This is the fifth volume in the present series.

The membership of the American Institute of Mining and Metallurgical Engineers totals approximately 9000, of whom some 1500 are members of the Institute of Metals Division. Each member of the Division receives not only the general volume of TRANSACTIONS of the Institute and this volume devoted to the Institute of Metals Division, but also MINING AND METALLURGY, published monthly, data sheets on nonferrous metals and pamphlets called TECHNICAL PUBLICATIONS, as they are issued. These TECHNICAL PUBLICATIONS constitute, in fact, additional copies (without discussions) of a majority of the papers incorporated in this volume. The cost of this duplication is considerable, not only in actual printing costs but in headquarters expense incurred in distribution. For reasons of economy, therefore, it has been deemed advisable in a few instances to incorporate papers in TRANSACTIONS but not to distribute them in T. P. form. In such cases, however, reprints in pamphlet form are available at headquarters and are supplied on specific request. Examples in this volume are the papers by Westgren, Sachs, Wever, Crane, Knerr and Sivil.

Two papers presented at the September, 1930, and February, 1931, meetings and not included in this volume were published in MINING AND METALLURGY and are referred to in the Contents and in the Index.

For a number of years, these volumes have contained practically all of the technical papers and their discussions presented at the two regular meetings each year, together with a list of the officers of the Institute and the officers and membership of special committees of the Division. It has not been the practice to incorporate in this volume such items as minutes of meetings or reports of officers and committees. Some brief reference to these items will be found occasionally in the general volume of TRANSACTIONS which is received by each member.

The By-laws of the Division as adopted at the February, 1930, meeting are also included in this volume. The preparation and adoption of these By-laws represent to some extent the efforts made during recent years to standardize the organization and procedure of the Division and provide for its healthy growth by systematic methods of selection, nomination and election of officers and members of the executive committee.

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By-laws of the Institute of Metals Division

[As Adopted February 30, 1930.]

Article I—Name and Object

Sec. 1. This Division shall be known as the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

Sec. 2. The object of the Division shall be to furnish a medium of cooperation between those interested in the metallurgy, fabrication and uses of the nonferrous metals and their alloys; to represent the A. I. M. E. in so far as nonferrous metallurgy is concerned, within the rights given in A. I. M. E. By-law XI., Sec. 1, and not inconsistent with the Constitution and By-laws of the A. I. M. E.; to hold meetings for social intercourse and the discussion of nonferrous metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on nonferrous metallurgy; to reject or accept such papers for presentation before meetings of the Division.

Article II—Members

Sec. 1. Any Member, Associate, or Junior Associate of the A. I. M. E. in good standing may become a Member, Associate or Junior Associate of this Division upon registering in writing a desire so to do, but without additional dues.

Sec. 2. But no one who has been continuously indebted to the A. I. M. E. or to this Division for more than three months shall be entitled to vote or to receive publications to which, as a member of the Division, he would be entitled.

Article III—Funds

Sec. 1. The expenditure of the funds received by the Division shall be authorized by the Executive Committee of the Division.

Article IV—Meetings

Sec. 1. The Division shall meet at the same time and place as the annual meeting of the A. I. M. E., and at such other times and places as may be determined by the Executive Committee subject to the approval of the Board of Directors of the A. I. M. E.

Sec. 2. The annual business meeting for election of officers shall be held within a few days before or after the annual business meeting of the A. I. M. E.

Sec. 3. At any meeting of the Division for which notice has been sent to the members of the Division through the regular mail at least one month in advance, a business meeting may be convened by order of the Executive Committee, and any routine business transacted not inconsistent with these By-laws or with the Constitution or By-laws of the A. I. M. E.

Sec. 4. For the transaction of business, the presence of a quorum of not less than 25 members of the Division shall be necessary.

Article V—Officers and Government

Sec. 1. The officers of the Division shall consist of a Chairman, two Vice-chairmen, Secretary and Treasurer. The office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

Sec. 2. The government of the affairs of the Division shall rest in an Executive Committee, in so far as is consistent with the By-laws of the Division and the Constitution and By-laws of the A. I. M. E.

Sec. 3.   The Executive Committee shall consist of the Chairmen, two Vice-chairmen, Past-chairman, Secretary, and nine members, all of whom shall be nominated and elected as provided hereafter in Article VII.

Sec. 4.   The Chairman and Vice-chairman shall serve for one year each, or until their successors are elected.   Each member of the Executive Committee (subsequent to the initial Executive Committee) shall serve three years. The Chairman shall remain a voting member of the Executive Commitee for one year after his term as Chairman.

Sec. 5.   The Treasurer of the Division shall be invited to meet with the Executive Committee, but without ex-officio right to vote.   He shall be appointed annually by the Executive Committee, from the membership of the Executive Committee or otherwise.

Article VI—Committees

Sec. 1.   There shall be two standing committees as follows: Papers Committee and Auditing Committee, and such other committees as the Executive Committee may appoint.

Sec. 2.   It shall be the duty of the Papers Committee to secure the presentation of papers of appropriate character at meetings of the Division and of the A. I. M. E.

Sec. 3.   It shall be the duty of the Auditing Committee to audit the accounts of the Division and report to the Executive Committee prior to the annual meeting of the Division.

Article VII—Nominations and Elections of Officers and Committees

Sec. 1.   Every year the Division shall elect a chairman, two vice-chairmen, a secretary and three members of the Executive Committee.

Sec. 2.   A nominating committee of five members of the Division shall be appointed by the Executive Committee immediately after the annual meeting.

Sec. 3.   This Committee shall make its report to the Executive Committee at or before the autumn meeting of the Division.

Sec. 4.   Any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than the date of the autumn meeting, and the persons so nominated shall be included in the official ballot.

Sec. 5.   The voting shall be by letter ballot.

Sec. 6.   The ballots shall be counted by a committee of tellers appointed by the Executive Committee.

Article VIII—Amendments

Sec. 1.   Proposals to amend these By-laws shall be made in writing to the Executive Committee and signed by at least ten members.   They shall be considered by the Executive Committee and announced to the members through the columns of *Mining and Metallurgy,* together with any comments or amendments made by the Executive Committee thereon.   They shall be voted upon at the annual meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

by different investigators, studying the same system independently, are very divergent.

Naturally, this does not entitle us to draw the conclusion that metal microscopy and thermal analysis are inadequate as methods. But it is evident that these tools of investigation must be applied with great care—which has not always been the case—and that they require much work and practical experience in order to avoid misinterpretation of the observations made. Further, it seems clear that if metallography in the future had recourse only to these pioneering methods, the general mapping out of the alloy equilibrium conditions would require a long time and much work.

Fortunately, the situation has changed now. In the methods of X-ray crystallography, metallography has found a new means of investigating alloys, which in an excellent way supplements the older methods. As a matter of fact, alloy phases may be identified by means of X-ray analysis in a more reliable way than earlier. In most cases X-ray investigation is able to give full evidence regarding the number of phases that occur in an alloy system, at least when it so happens that they are stable at ordinary temperature. Further, their composition may generally also be found out in this manner, and the extent of their homogeneity ranges in many cases determined with a very high degree of accuracy.

To all these advantages, possessed by X-ray methods, as a means of analytic investigation of intermetallic phases, may also be added another very important one. The X-ray interferences give evidence regarding the crystal structure of the different alloy phases, and this provides a certain insight into their chemical characteristics, which the earlier metallographic methods could do but very incompletely. Certain laws governing the coupling of metal atoms into combined phases have been traced thereby, and structure analogies have been proved to exist between different alloy systems. The intermetallic reaction products are not formed so capriciously as believed earlier, but instead, in many cases, a certain simple relation seems to exist between crystal structure and the properties of its constituent atoms. Therefore the knowledge gained by the X-ray analysis of one system may often be of use for investigating another. The determinations of the constitution of different alloys therefore support each other nowadays to a far greater extent than in former years.

PHRAGMÉN'S FOCUSING CAMERAS

The X-ray methods applied today are known so generally that a report of them is unnecessary here. However, as the powder photograms that accompany this paper do not belong to the usual type, a short description will be given of the cameras with which they were obtained.

These cameras were constructed by G. Phragmén, with whom the author has had the invaluable advantage of cooperating for many years.

The cameras are constructed according to a principle earlier applied for the same purpose by H. Seemann and H. Bohlin[1], which is illustrated in Fig. 1.   Rays that start from one and the same point of a cylinder surface, and which are orientated in a plane at right angles to the axis of this surface, are reflected at the same angle in such a way that they unite again at another point of the cylinder surface.   In order to provide a sufficiently sharp focusing, Phragmén made the following arrangement.   The slit through which the X-rays enter the camera has been made only about 0.2 mm. wide (length about 1.5 mm.).   The beam has been limited by means of a special diaphragm between the slit and the illuminated preparation.   Further, the diffraction range has been divided among three different cameras, whereby a larger radius has been allowed for the one intended for the least deviated interferences than for the two others.   The radius of this so-called inner camera is 85 mm., while
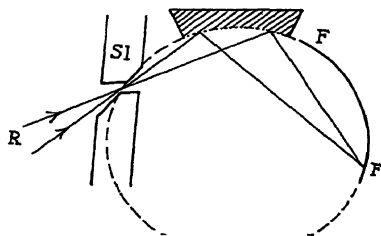
FIG. 1.— FOCUSING PRINCIPLE (SEEMANN AND BOHLIN).
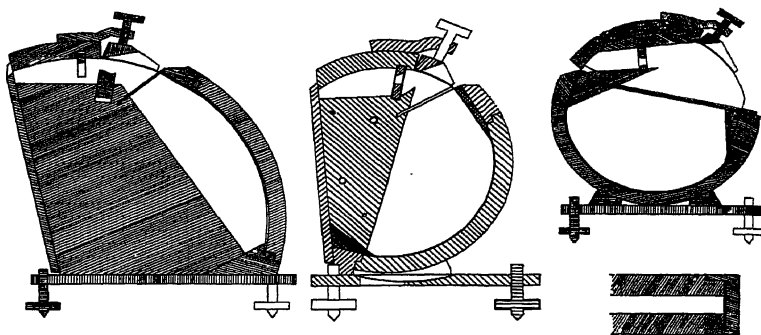
FIG. 2.—CONSTRUCTION OF FOCUSING CAMERAS.

that of the middle camera, embracing the middle of the diffraction range, is 48 mm.; the outer camera for the most deviated interferences has a radius of 42 mm.   Naturally, the diffraction ranges of the different cameras overlap each other to a certain extent.   The construction of the cameras is shown in Fig. 2 and photographs are given in Figs. 3 and 4.

The specimen intended for investigation is fastened by means of some adhesive to an unsized piece of paper, which is pressed against the

[1] H. Seemann: *Ann. d. Physik* (1919) **59,** 455.
H. Bohlin: *Ann. d. Physik* (1920) **61,** 430.

cylindrical surface of the camera by a special holder that is retained in its proper position by means of a screw.   The photographic film is pressed against the cylinder surface by a lid that is fastened with hooks; on the outer camera this lid is fastened to the foundation, while it is detachable on the others.

In Fig. 5, X-ray patterns of γ brass, taken in these cameras, are compared to a photogram of the same substance obtained in a camera of the ordinary round type (film diameter, 55 mm.).   The time of exposure was
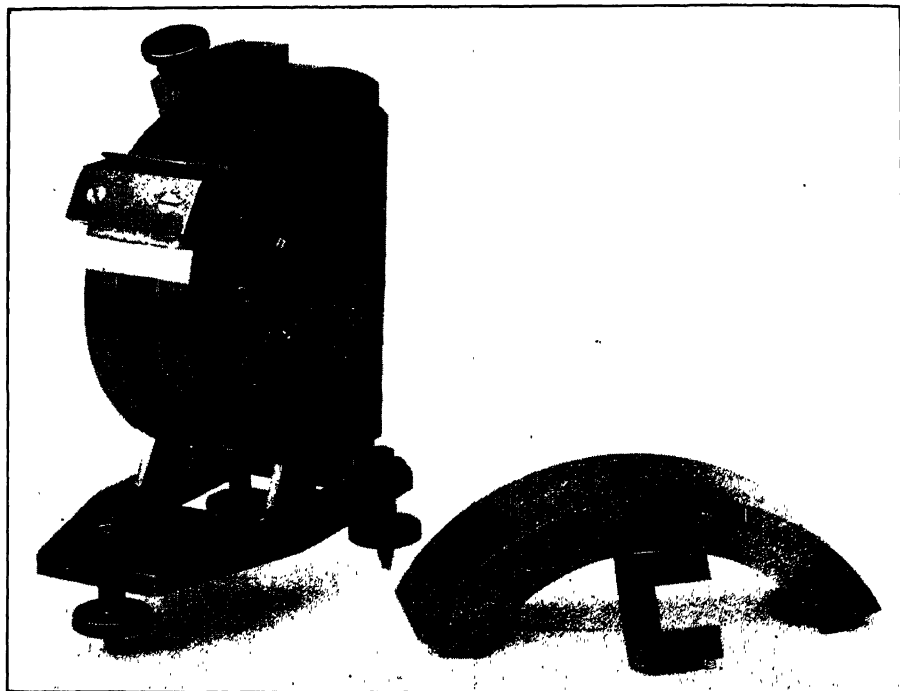
FIG. 3.—FOCUSING CAMERA.

about the same for all these photograms, and, as will be seen, the power of dispersion of the focusing cameras is considerably greater than that of the ordinary round type.

The edges of the shade caused by the continuous radiation are used as reference lines for measuring the photograms.   In order to make these lines sharply defined, pieces of hardened steel with ground edges have been let in at the ends of the exposure aperture of the cameras.

The cameras are calibrated by means of sodium chloride, the standard substance of X-ray spectroscopy.   Thus a table is compiled for each camera from which the $\sin^2 \dfrac{\theta}{2}$ values (θ = the angle of deviation) may be

read directly for each interference line when its distance to the edge of the continuous blackening of the film has been measured. When measuring the film, correction is made for its eventual shrinking or lengthening by comparing the length of the shade with the standard extension of it, on which the calibration table is based.
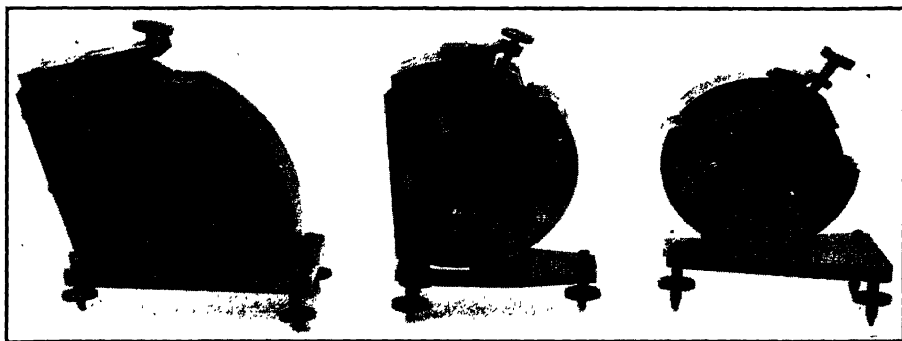
FIG. 4.—FOCUSING CAMERAS.

The linear dimensions of crystal lattices may be determined in these cameras with an accuracy of which the mean error certainly does not exceed 0.1 per cent. By narrowing the slit and increasing the time of exposure, together with a specially careful measuring of the film, the accuracy may still be considerably increased if this is necessary for some special purpose.
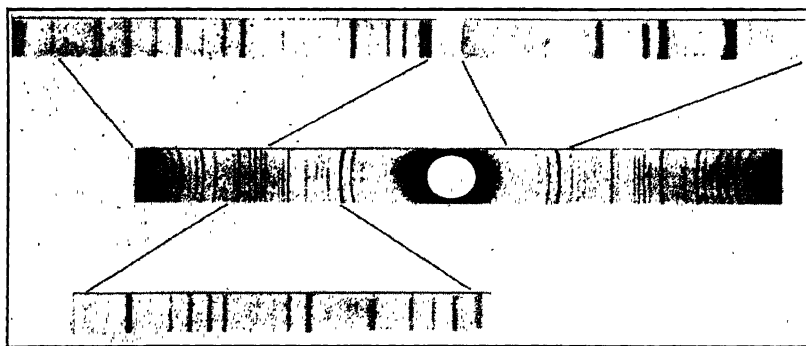
FIG. 5.—PHOTOGRAMS OF γ BRASS OBTAINED BY MEANS OF PHRAGMÉN'S FOCUSING CAMERAS COMPARED WITH AN ORDINARY PHOTOGRAM OF THE SAME SUBSTANCE. FE-K RADIATION.

PREPARING SAMPLES FOR X-RAY ANALYSIS

An advantage which the X-ray methods offer compared to the older ways of metallographic investigation is that they require comparatively

small quantities of substance for their application.   The amount of alloy needed for an analysis may therefore, in many cases, be made simply by the melting together of weighed quantities of the components in small, evacuated glass or quartz tubes.   Perfectly pure alloys with an accurately known composition are produced thereby, provided the metals do not react with the tube material.

Eventual segregation in the specimens generally affects the sharpness of the X-ray photograms unfavorably; if the composition of a phase is not identical in all parts of a specimen it will in most cases cause diffuse interference lines.   The heat treatment of the specimens, necessary for eliminating segregation effects, is easily brought about, however, if the specimens are tempered for some time in evacuated glass or quartz tubes, thus being protected against oxidation during this process in an effective and simple way.

The homogeneous lattice regions, in a specimen that has been reduced to powder by means of filing or crushing, generally are so small, on account of the very severe cold working, that the lines in its powder photogram become diffuse.   Before a photogram is taken of an alloy powder, it ought therefore to be recrystallized by tempering at a suitable temperature.   The restoration of the deformed crystal grains usually is accomplished in the course of a few minutes, if the temperature is sufficiently high.   In the case of an alloy powder containing several phases it is not to be imagined, however, that when the recrystallization has been completed, an equilibrium corresponding to the temperature to which the specimen has been heated has really been reached.   For attaining equilibrium it is often necessary that certain diffusion processes be given time for completion.   The tempering, therefore, must not be too short if equilibrium is to be reached.   How long it ought to be is, of course, principally dependent on how much below the melting point of the specimen the temperature lies, and further, on how fine and intimate the mixture is in which the phases appear in the powdered grains.

After the tempering, the equilibrium that has been attained in the specimen may be fixed, in most cases, through quenching.   As the alloy is investigated in a powdered condition, a fixation of its state through rapid cooling may be made very effective.   If it is heated in a glass tube this will crack when immersed in water and the powder will be cooled very rapidly.   If the powder has been enclosed in a quartz tube during the tempering, the tube must be broken the moment it is immersed in the quenching fluid.   It may happen that the investigation is complicated by the partial oxidation of the specimen during this treatment, but as a rule the oxidation is so slight that it does not cause any extra lines in the photograms.

The fact that the alloys may be investigated in a powdered condition is advantageous not only because powder may be quenched more effec-

tively than whole pieces but also because the chemical character of the residue which may remain after a partial dissolution of alloys, containing several phases, in acids or other solvents, may be identified by X-ray analysis. The phase that is most resistant against the attack of the solvent may be concentrated in this way. Even if the amount contained in the alloy is so slight that its interferences do not appear in the diffraction patterns of the alloy itself, it may still be identified by the X-ray photograms of the residue formed during the dissolution. In this residue, however, the phase may often be admixed with larger or smaller amounts of solid dissolution products. Consequently, as we know, the information concerning the nature of this phase, gained by a chemical analysis of the powder as a whole, is uncertain. In these photograms, however, the interference series, characteristic of the phase appears, and by comparing this series with photograms of known alloy phases, which may be expected to occur in the alloy in question, the isolated phase may be identified. This method is especially suitable for investigating carbide phases in alloy steels. The carbide crystals which are contained in the sediment formed by the dissolution of steels in dilute acids are generally small and well defined as to their composition, besides not having been subjected to any cold working. Such powders, therefore, generally give excellent photograms.

IDENTIFICATION OF ALLOY PHASES BY MEANS OF X-RAY INVESTIGATION

One of the pioneers in the field of X-ray crystallography, Dr. A. W. Hull, pointed out, shortly after his first publication concerning the powder method had appeared, that this method provided a new means of chemical analysis.[2] A powder photogram of a mixture of crystallized substances contains line series corresponding to every one of these, provided their relative amount is sufficient. The X-ray interferences thus enable us to identify the different phases of a mixture. It is upon this principle that the X-ray analysis of alloys is based.

Its application to a simple case is exemplified in Fig. 6, showing a series of photograms of gold-antimony alloys. As will be seen, only one intermediate phase, $AuSb_2$, occurs in this system. Only three line series appear, corresponding to Au, $AuSb_2$ and Sb. In this case the data given in the literature have been fully corroborated. The phases must be practically insoluble in each other, as the position of the interference lines does not vary in the different photograms.

Systems of this simple kind are fairly rare. As a rule, the homogeneity ranges of the different phases are more extended; for instance, the case in the well-known copper-zinc system, of which the photogram series is given in Fig. 7. With rising zinc content the interference lines within each homogeneity range are here displaced towards smaller devia-

[2] A. W. Hull: *Jnl.* Amer. Chem. Soc. (1919) 41, 1168.

tion angles, which shows that the lattice dimensions within these intervals grow with an increasing zinc content. Only within the two-phase ranges they remain independent of the composition. They may, however, vary with the temperature, as the saturation concentration of the phases in equilibrium may change on heating or cooling. These facts will be discussed later in the paper.

An X-ray analysis made several years ago showed that the copper-zinc system contains several different phases. After the face-centered cubic copper phase, α, comes another one, β, the composition of which corresponds approximately to CuZn, built up of two simple cubic lattices centering each other. From analogous phases, occurring in the Ag-Zn and Au-Zn systems, we may infer that one of these lattices holds mainly the copper atoms, the other mainly the zinc atoms. After this phase, appears γ, possessing a complicated cubic structure with 52 atoms in the elementary cube. Then follows a close-packed hexagonal phase, ϵ,
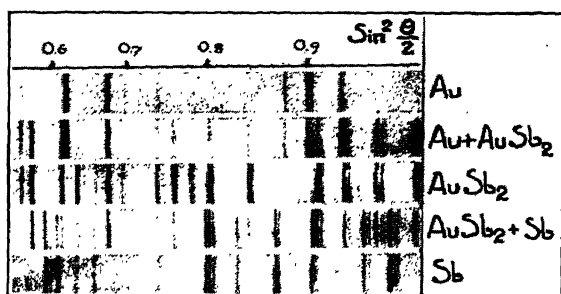
FIG. 6.—POWDER PHOTOGRAMS OF GOLD-ANTIMONY ALLOYS. FE-K RADIATION.

with an axial ratio of about 1.6, and finally the zinc phase η, also hexagonal and of the same kind as ϵ though having an axial ratio which amounts to about 1.9.

In order to verify these results, new photograms of copper-zinc alloys have recently been taken with the focusing cameras, some of them being the diffraction patterns given in Fig. 7. Here may be seen the five different interference series that were observed in the older photograms, but also a sixth line series, in the range between the β and γ phases. Thus, the X-ray analysis has given evidence of the occurrence of a phase in the copper-zinc system which was overlooked in earlier investigations. Its X-ray pattern does not differ very much from that of the γ phase, which, of course, is the reason why it was not noticed in the earlier photograms. Where the γ phase has single interferences this newly detected substance—which, owing to its similarity to γ, may be denoted adequately as γ'—generally has multiples. It is evident that we are dealing here with a kind of crystal, the structure of which differs but

slightly from the γ phase. It may be taken as derived from the same, and as a result of a slight deformation of its lattice. Its symmetry evidently is not cubic but probably tetragonal, hexagonal or possibly orthorhombic. As a matter of fact, the phenomenon encountered here is very common in alloy systems.

In the copper-aluminium system, there is a phase of which the structure is analogous to that of γ brass. It is cubic, and its elementary cube
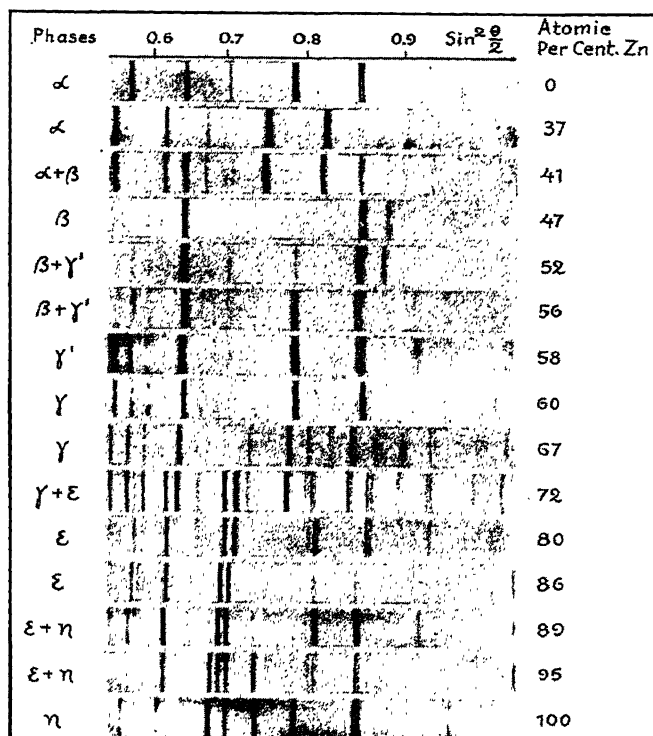
FIG. 7.—POWDER PHOTOGRAMS OF COPPER-ZINC ALLOYS. FE-K RADIATION.

contains 52 atoms.[3] However, the two kinds of atoms are here apportioned to lattice points in such a way that the lattice becomes simple cubic, while γ brass has a body-centered structure. The fundamental lattice is identical in the two cases; the lattices differ only with respect to their "superstructure." The copper-aluminum phase is homogeneous within the interval 31 to 35 atomic per cent. aluminum; i. e., the elementary cube contains at one of its concentration limits a group of atoms corresponding to the formula $Cu_{36}Al_{16}$, at the other a group corresponding

[3] E. R. Jette, G. Phragmén and A. F. Westgren: *Jnl.* Inst. Metals (1924) **31**, 201.

to $Cu_{34}Al_{18}$. As may be seen in the photograms in Fig. 8, the alloys within this interval give rise to simple interference lines; within the entire range the symmetry is cubic.   If the aluminum content is increased to above 35 atomic per cent., however, most of the lines first become diffuse; at a still higher concentration of aluminum they split up, forming distinct multiples.   The variation which takes place in the properties of the alloys with the changing composition appears to be quite continuous here, so that we might be disposed to assume that it is one and the same phase with which we are dealing.   A decrease in symmetry, however, is in itself a discontinuous phenomenon, so that it would appear correct to assume that a two-phase range actually does exist at about 35 atomic

FIG. 8.—POWDER PHOTOGRAMS OF COPPER-ALUMINUM ALLOYS IN RANGE OF 31 TO 50 ATOMIC PER CENT. AL.   FE-K RADIATION.

per cent. Al, although it is so narrow and the difference between the coexisting phases so slight, that its existence is very difficult to establish.[4] At 45 atomic per cent. Al, lines show up belonging to a new phase.   They become more distinct as the aluminum content rises and they have their maximum of intensity at 50 atomic per cent. Al.   No displacement of the position of the lines may be observed when the concentration 50 atomic per cent. Al is surpassed.   It is evident, therefore, that they emanate from a phase which may be indicated as CuAl.   Crystals of this kind have been investigated by G. Phragmén by means of the Laue

[4] Cf. Investigations by Einar Öhman and Elis Persson regarding the Fe-Mn and the Cu-Mn systems.   *Ztsch. f. phys. Chem.* (1930) **B8**, 81; (1930) **9**, 25.

pattern and rotation method, and he was able to state that this phase has a very complicated orthorhombic structure. Its elementary cell contains about 1500 atoms.

Phases with so-called γ structure—whose fundamental lattices are analogous with that of γ brass—have been encountered in a great number of alloy systems. In many of these a decrease in symmetry at one of the limits of the homogeneity range has been observed, of the same kind as that found in γ brass and the γ phase of the Cu-Al system. This is, for instance, the case in the nickel-zinc system.[5]
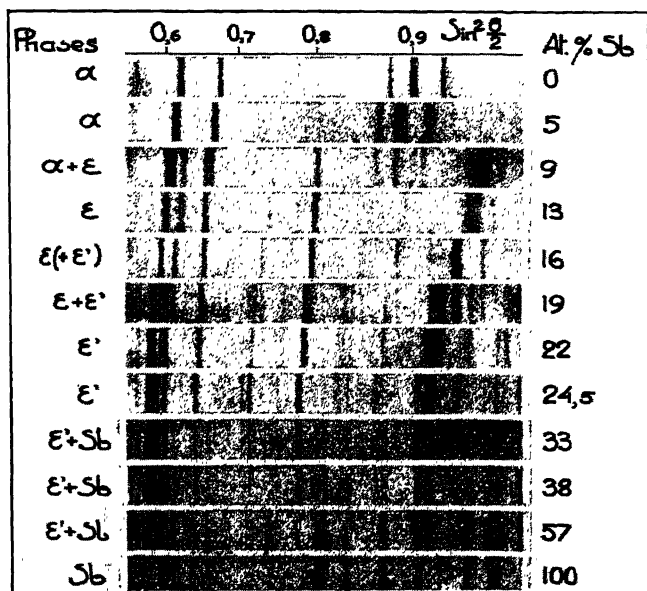

FIG. 9.—POWDER PHOTOGRAMS OF SILVER-ANTIMONY ALLOYS. FE-K RADIATION.

The γ phases are not the only ones possessed of this peculiarity. Even phases with close-packed hexagonal structure—which, as we know, also occur frequently in alloys—may in certain systems coexist with a crystal species, the atomic grouping of which differs but slightly from their own.

An equilibrium of this kind was encountered for the first time in the silver-antimony system.[6] A series of photograms of silver-antimony alloys is given in Fig. 9. In this system the hexagonal close-packed phase occurs within the interval 10 to 16 atomic per cent. Sb. As seen in Fig. 9, its diffraction pattern is simple. Photograms of a similar

[5] A. Westgren and W. Ekman: K. Vetenskapsakademiens Arkiv för kemi etc. (1930) **B10**, No. 11; W. Ekman: Ztsch. f. phys. Chem. (1931) **B12**, 57.
[6] A. Westgren, G. Hägg and S. Eriksson: Ztsch. f. phys. Chem. (1929) **B4**, 453.

character are obtained also from alloys within the interval 20 to 25 atomic per cent. Sb. The only distinct difference is that some of the interferences of the latter are resolved into doublets.   A closer inspection of the last-mentioned photograms has shown that the atomic grouping of the phase in question corresponds with the one shown in Fig. 10.   It is orthorhombic with four atoms in the unit cell.   If the ratio of the basal edges were $\sqrt{3}:1$, the structure would be a close-packed hexagonal one, with an ensuing atomic grouping identical with that occurring in the interval 10 to 16 atomic per cent. Sb.   The axial ratio, however, is not exactly $\sqrt{3}:1$; *i. e.*, not 1.732:1 but 1.743:1.   The photogram of the alloy containing 19 atomic per cent. Sb in Fig. 9 shows that although the two phases differ but slightly as regards their atomic grouping, their homogeneity ranges are separated by a distinct two-phase interval.

A phenomenon quite identical to the one described here has been reported by Gunnar Hägg as a result of a very careful X-ray analysis of the Fe-N system.[7] Within the interval 8 to 11 per cent. N in this system a phase occurs in which the iron atoms are arranged in a close-packed hexagonal lattice.   The compound Fe_2N, with a nitrogen content of 11.2 per cent., however, possesses an orthorhombic pseudohexagonal structure of quite the same kind as the one encountered within the interval 20 to 25 atomic per cent. Sb in the silver-antimony alloys.   The ratio of the basal edges of the orthorhombic unit cell was even found to be practically identical for the Fe-N phase and for the Ag-Sb alloy; in the former case, 1.744:1.
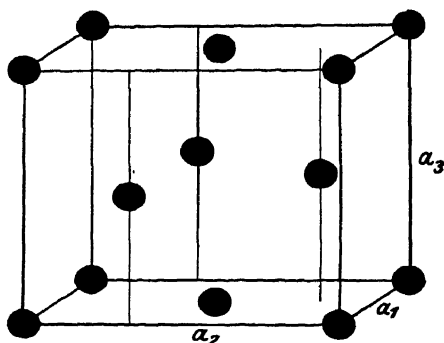

FIG. 10.—ATOMIC GROUPING OF PHASE ϵ' OF SILVER-ANTIMONY SYSTEM.

According to recent investigations by O. Nial and A. Almin the same phenomenon is encountered also in the silver-tin system.   The photograms of these authors are given in Fig. 11.   In full agreement with microscopic observations made by A. J. Murphy[8] they have found here that two intermediate phases occur in this system.   At the crystallization temperature used, 450° C., one phase is homogeneous within the interval 13.5 to 20.5 atomic per cent. Sn, the other within a narrow range, slightly below and close to 25 atomic per cent. Sn.   The former of these phases has a close-packed hexagonal lattice while the structure of the latter is almost identical, being pseudohexagonal orthorhombic.

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[7] G. Hägg: *Nova Acta* Reg. Soc. Sci. Upsaliensis [4] (1929) **7**, No. 1; *Ztsch. f. phys. Chem.* (1930) **B8**, 455.

[8] A. J. Murphy: *Jnl.* Inst. Metals (1926) **35**, 107.

The ratio of the basal edges of the unit cell in this case, however, does not exceed $\sqrt{3}:1$, but is slightly less; i. e., 1.724:1.

The examples cited, regarding the progress made by X-ray methods in the investigation of the constitution of alloys, may perhaps appear only to pertain to details, the importance of which cannot be estimated yet but the studies of alloy equilibrium diagrams by means of X-ray analysis has shown that many of them have to be thoroughly revised. In many cases, phases have been detected which cannot, like the above, be considered as pertaining to known phases, but which possess a structure
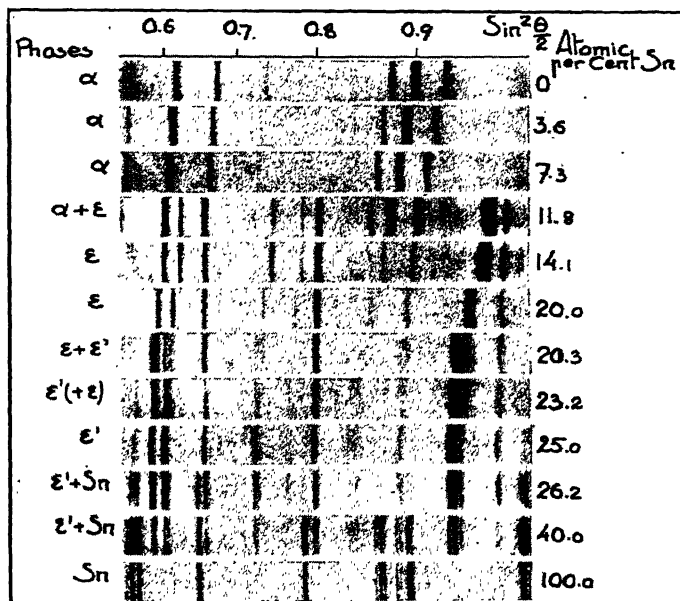

FIG. 11.—POWDER PHOTOGRAMS OF SILVER-TIN ALLOYS (O. NIAL AND A. ALMIN). FE-K RADIATION.

quite different from these. Thus an X-ray analysis of the gold-cadmium system by E. R. Jette indicated that it contains no less than nine intermediary phases while an investigation made recently with the aid of older metallographic methods has proved the existence of only five of them. William F. Ehret has recently taken X-ray photograms of iron-tin alloys which show that the equilibrium diagram of the Fe-Sn system, given a few years ago by F. Wever, and which was based on thermal-analytical and microscopical investigations,[9] must be completed with at least three new phase ranges. Sven Arrhenius, by means of X-ray analysis, has detected a new phase in the copper-silicon system, which holds 10 per cent. Si and which is stable at ordinary temperature. This

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[9] F. Wever and W. Reinecken: *Mitt.* K-W. Inst. f. Eisenforsch. (1925) **7**, 69.

phase has been overlooked in all previous investigations concerning this system. These examples will suffice to show that X-ray methods certainly may be of use in studying the alloy equilibrium diagrams.

One of the most important uses of X-ray analysis as a means of identifying alloy phases comes in when it is applied to the investigation of residues, obtained after a partial dissolution of alloys in acids. As an example of this, some photograms of carbide powders, isolated from certain steels, are given in Fig. 12. By comparing these with the diffraction patterns of known carbides, also presented in Fig. 12, it has been possible to determine the exact character of the carbide phases present in these steels. Thus it is clear that the carbide of a ball-bearing steel
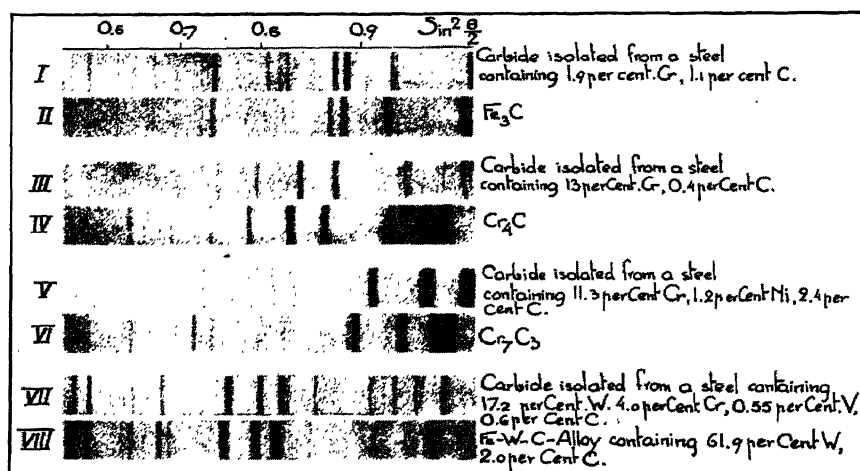

FIG. 12.—POWDER PHOTOGRAM OF STEEL CARBIDE PHASES.
I–VI, Cr-K radiation; VII–VIII, Fe-K radiation.

(containing 1.1 per cent. C, 1.9 per cent. Cr) is cementite. We may here even infer from the displacement of the interference lines that the iron atoms have been partly substituted by chromium atoms. The carbide phase of a stainless steel with 13 per cent. Cr, 0.4 per cent. C, consists of a cubic chromium carbide Cr_4C, in which approximately one-third of the chromium has been replaced by iron. Likewise, it has been proved that a steel containing about 11 per cent. Cr, 1.2 per cent. Ni and 2.4 per cent. C contains a trigonal carbide Cr_7C_3 in which more than one-half the content of chromium is replaced by iron.[10] Finally, the residue resulting after a dissolution of a high-speed steel in dilute acid gave the same photogram as an iron-tungsten-carbon alloy, the composition of which[11]

[10] A. Westgren, G. Phragmén and Tr. Negresco: *Jnl.* Iron and Steel Inst. (1928) **117**, 283.

[11] A. Westgren and G. Phragmén: *Trans.* Amer. Soc. Steel Treat. (1928) **13**, 539.

corresponds approximately to the formula Fe_4W_2C. This new and improved kind of residue analysis has also already been applied successfully to other alloys than steel.

X-RAY DETERMINATION OF THE HOMOGENEITY RANGES IN EQUILIBRIUM DIAGRAMS

As pointed out above, the displacement of the interference lines with change in composition, found in homogeneity ranges of different alloy phases, provides a means of estimating the extent of these intervals. Certain doubts have been expressed as to the justification of this procedure[12] but a comparison between these concentration values and values obtained in other ways—for instance, the data resulting from reliable microscopic observations—has always verified their correctness.
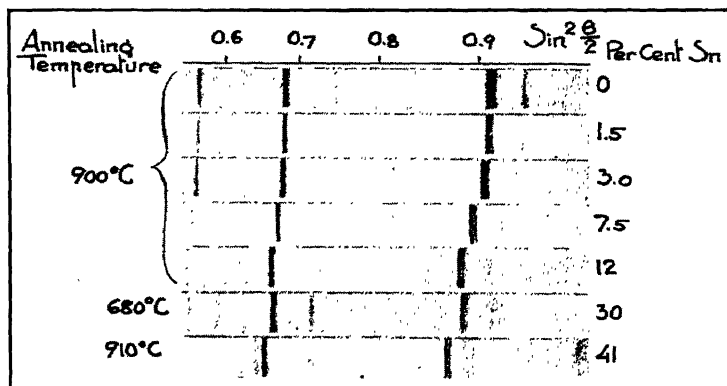

FIG. 13.—POWDER PHOTOGRAMS OF IRON-TIN ALLOYS (W. F. EHRET). FE-K RADIATION.

Thus if the photogram series in Fig. 7 is used for determining the limiting concentrations of the Cu-Zn phases occurring at the temperatures at which the recrystallization of the alloy specimens used has taken place values will result which fully agree with the prevalent equilibrium diagram of this system which has been established in a very accurate way in consequence of numerous studies.

It has been shown recently, by N. Ageew and G. Sachs,[13] in a treatise concerning the solubility of copper in silver, that the study of the position of the X-ray interferences affords a means of determining, in detail, and very accurately, the variation of the saturation concentration with the temperature. It is evident from this investigation that often the satura-

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[12] W. Rosenhain: *Jnl.* Inst. Metals (1929) **42**, 54.
[13] N. Ageew and G. Sachs: *Ztsch. f. Physik* (1930) **63**, 293.
N. Ageew, M. Hansen and G. Sachs: *Ztsch. f. Physik* (1930) **66**, 350.

tion limits actually may be determined more accurately by means of X-ray methods than by microscopic examination—a view which has also been corroborated by personal experience of the author.

In Fig. 13 has been plotted a series of photograms of Fe-Sn alloys, taken by W. F. Ehret. The specimens, containing 0 to 12.1 per cent. Sn, were annealed for one week at 900° C., with the view of eliminating segregation, and after that were quenched in water. After this treatment they all consist of a homogeneous solid solution of tin in iron. The displacement of the interferences with a rising content of tin shows how the lattice grows as the Fe atoms are replaced by Sn atoms. In the two last photograms in Fig. 13 lines occur which do not belong to the iron phase and which show that the saturation limit of this phase has been exceeded. One of the later X-ray photograms corresponds to an
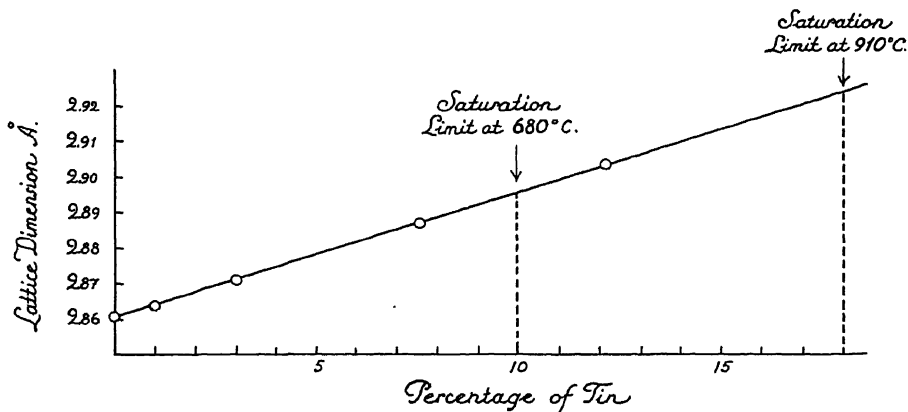

FIG. 14.—VARIATION OF LATTICE DIMENSIONS WITH TIN CONTENT IN α IRON PHASE

alloy with 30 per cent. Sn, which has been tempered at 680° C. for four days and then quenched in water; the other corresponds to an alloy holding 42 per cent. Sn which was annealed for 5 min. at 910° C., followed by an identical sudden quenching. The positions of the interferences are not identical in the two photograms, and we may therefore conclude that the tin content is not the same in the phase saturated at 680° C. and the one saturated at 910°. The parameter of the former is 2.895 Å, of the latter 2.924 Å. According to the curve given in Fig. 14, representing the variation of the parameter with the change in composition, the first value corresponds to a tin concentration of 10 per cent. The relation between the parameter and the composition seems in this case to be practically linear, and if we assume that this is also the case for tin concentrations exceeding 12.1 per cent., an extrapolation of the curve in Fig. 14 made accordingly would give a tin content of 18 per cent. of the iron phase saturated at 910° C. If for some reason we should wish to make a

closer study of the variation of the solubility of tin in iron, this would, of course, be easy, by introducing a few more points into the diagram of Fig. 14, so as to fix the curve more accurately for even higher percentages of tin, and also by determining the saturation limit at several different temperatures.

The possibility of applying X-ray methods for determining saturation limits of alloy phases may sometimes be restricted on account of difficulties in bringing about equilibrium or else because of the impossibility of fixing this condition by means of quenching. In spite of the quenching being very sudden, one phase may separate from another, or some other reaction may take place. The composition of the crystal species in the specimen will be varied thereby and the interferences consequently will be diffuse. These phenomena, which have caused great difficulties in certain cases, fortunately are seldom met with.
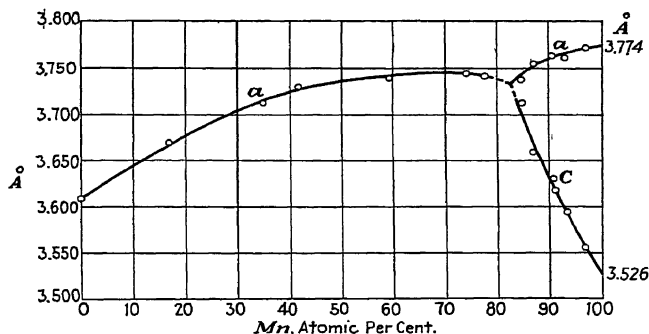

FIG. 15.—VARIATION IN LATTICE DIMENSIONS OF FACE-CENTERED CUBIC COPPER PHASE AND PSEUDOCUBIC FACE-CENTERED TETRAGONAL γ MANGANESE PHASE, COPPER-MANGANESE SYSTEM.

Naturally, the possibility must also be taken into consideration that the atomic dimensions of the components entering a system may differ from each other but slightly. The change in the lattice dimensions with the composition within the homogeneity ranges will then be slight, which renders the method of determining the position of the saturation limits by the displacement of the X-ray interferences insufficiently sensitive. Thus, in systems of this kind, which may be exemplified by Fe-P and Cu-Si, the circumstance that the interferences referring to a certain phase remain in an identical position whether they be in equilibrium with the one or with the other of the adjacent crystal species may not be taken as a proof of this phase having a restricted homogeneity range.

In certain rare cases a change of sign may happen as regards the variation of the lattice dimensions at a definite concentration within an extended homogeneity range; i. e., on increasing the content of one component, the parameter may at first increase and then decrease. Natu-

rally, in these cases—at least within certain concentration ranges—the composition of a phase cannot be derived from the lattice constants. During an X-ray analysis of the Cu-Mn system, Elis Persson recently came upon a case of this peculiar kind.[14]   The diagrams of the variation in lattice dimensions of the face-centered cubic copper phase, and the pseudocubic face-centered tetragonal γ manganese phase found by this author are given in Fig. 15.   Even the systems (Fe, Mn)$_3$C and (Fe, Cr)$_3$C show similar peculiarities.   This phenomenon has so far been encountered onl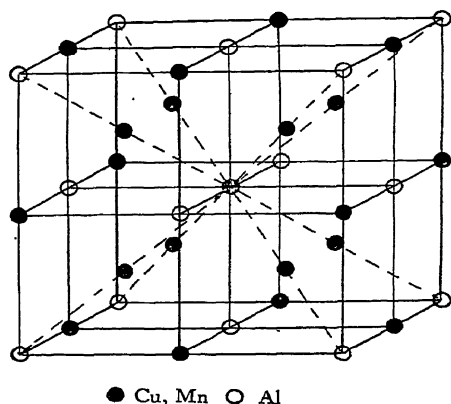y in systems that contain so-called transition elements—that is, metals whose atoms have incomplete inner electron shells—and it is probable that it may in some way be related to this peculiarity in atomic structure.

With the above restrictions, the X-ray methods have thus been found to be not only applicable but actually very valuable as a means of laying down the concentration limits in equilibrium diagrams of alloy systems.   In certain cases they have supplied important information concerning the constitution of alloys, where a persevering study by means of older methods has not been able to give satisfactory evidence regarding important points in their structure.   Thus, Elis Persson has attacked the problem of the constitution of the ferromagnetic Cu-Mn-Al alloys by means of X-ray methods, and it appears as though he had succeeded in definitely fixing the character of the phase which is possessed of the ferromagnetic properties.[15]

● Cu, Mn ○ Al

FIG. 16.—CRYSTAL LATTICE, COPPER-MANGANESE-ALUMINUM S Y S T E M WHEN MANGANESE VARIES FROM 6.5 TO 32.5 PER CENT.

This investigator has quenched a series of alloys—the compositions of which all correspond to the formula (Cu, Mn)$_3$Al with a manganese content varying within the interval 0 to 67 per cent.—from a temperature of approximately 50° below their melting point.   The alloys of which the manganese content exceeds about 20 per cent. have proved to be ferromagnetic.   Those which had a manganese content ranging within the interval 6.5 to 32.5 per cent. were, after microscopic as well as X-ray investigation, found to consist of practically one phase.   Judged by the photograms, the crystal lattice must here be of the kind seen in Fig. 16. The lattice parameter within this interval was found to increase with a

[14] E. Persson: *Ztsch. f. phys. Chem.* (1930) **B9**, 25.
[15] E. Persson: *Ztsch. f. Physik* (1929) **57**, 115.

rising manganese content, as shown in the curve in Fig. 17. From an extrapolation of the approximately rectilinear part of this curve we may infer that a homogeneous alloy with identical structure corresponding to the formula Cu_3Al ought to have a parameter of 5.833 Å and an alloy of the same kind, composed according to the formula Cu_2MnAl, a parameter of 5.950 Å.

The quenched alloy specimens were then tempered at 210° C. for 14 days. The result of the X-ray investigation was that the one of which the composition corresponded to Cu_2MnAl was unchanged. In the others, a separation into two phases had taken place. Two interference series, both of the same kind as those found in the quenched
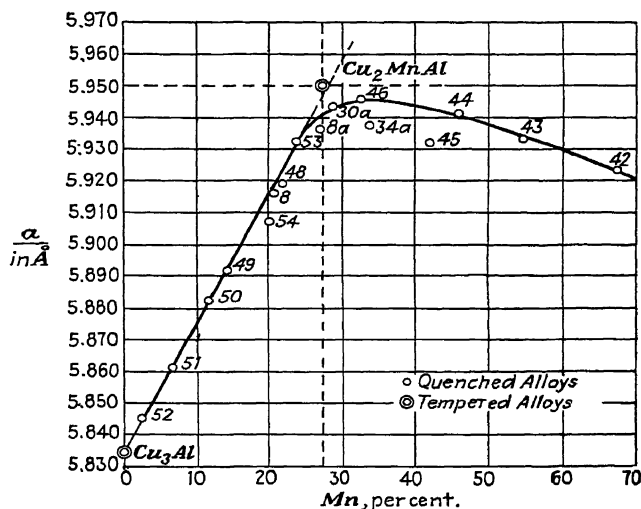

FIG. 17.—INCREASE OF LATTICE PARAMETER WITH RISING MANGANESE CONTENT.

specimens, i. e. corresponding to the structure type given in Fig. 16, were observed in the photograms. The parameter of the one was 5.833 Å, while that of the other was 5.950 Å. This shows that on annealing a phase Cu_3Al separates from the quenched specimens to such a degree that the composition of the remaining ternary crystal species will correspond to the formula Cu_2MnAl. The former is not stable below 570° C. but decomposes at this temperature if it has formed in a solidifying melt of copper and aluminum, even though the cooling be sudden, forming a mixture of the copper phase saturated with aluminum together with the crystal species Cu_9Al_4, mentioned above. As it is formed at a temperature as low as 210° C., its rate of decomposition is evidently so slow that it remains unchanged. It is evident that the ferromagnetic properties should be allotted to Cu_2MnAl, seeing that the magnetic property of these alloys varies in

proportion to the content of this phase.   It is probable that the man-
ganese atoms of this crystal species are arranged in a regular way in
relation to the copper atoms, so that the atomic grouping corresponds
to one of the alternatives given in Fig. 18. . Consequently, the magnetic
atoms would here be arranged in a face-centered cubic lattice.

Identical results were obtained by H. H. Potter[16] who has been study-
ing single crystals with the composition Cu_2MnAl by means of X-rays.
The magnetic properties of this alloy were found to vary with the orienta-
tion of the crystal axes in the magnetic field just as nickel crystals do.
No analogy with α iron crystals could be found in this respect.   Potter
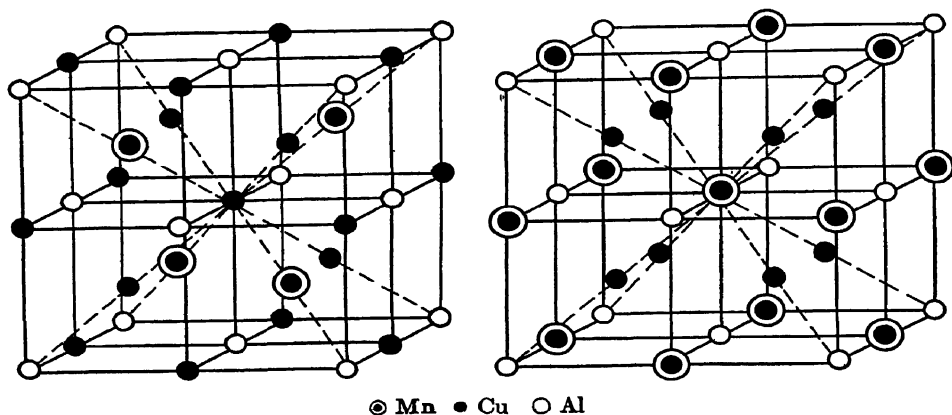

◉ Mn   ● Cu   ○ Al
FIG. 18.—POSSIBLE ATOMIC GROUPINGS OF Cu_2MnAl.

therefore inferred that the magnetic particles, *i. e.*, the manganese atoms,
in Cu_2MnAl are orientated in a face-centered cubic lattice.

INTERMETALLIC COMPOUNDS AND SOLID SOLUTIONS

Investigations regarding the constitution of alloys very often finish
with an attempt to state by means of chemical formulas which inter-
metallic compounds have been encountered.   For phases that possess
narrow homogeneity ranges and a composition corresponding to simple
stoichiometric proportions this is generally easily performed.   In the
cases of extended homogeneity ranges—which are by far more generally
encountered—recourse has to be taken to special expedients.   If the
liquidus curve within the interval shows a maximum, or if singularities
have been observed in the curves, indicating the variation of certain
properties with the composition—*e. g.*, the electrical conductivity—this
has been taken as a sign that the composition corresponding to such
points is of fundamental importance for the phase in question.   In the
cases where this composition corresponds to simple stoichiometric pro-

[16] H. H. Potter: *Proc.* Phys. Soc. [London] (1929) **41**, 135.

portions, the phase has generally been indicated with the corresponding formula. The fact that the homogeneity range has a certain extension has been explained by the assumption that the chemical compound found has the power of taking up a certain amount of the components or of other intermetallic compounds in solid solution. In the cases where even the indicated expedients have failed to give information regarding which compound a certain phase may represent, it has as a rule been considered merely as a solid solution.

These previous attempts at determining the chemical character of alloy phases have mainly implied an endeavor to apply to alloy research conceptions which have proved fruitful in other parts of chemistry. It is, however, difficult to classify the alloy phases into chemical compounds and solid solutions. In so far as this classification really has been carried through, it has only very slightly increased our knowledge regarding intermetallic reactions.

Despite this, the author, in cooperation with G. Phragmén, has made an attempt to bring the older mode of classifying alloy phases in harmony with the one which has arisen as a result of the X-ray analytic results.[17] It is characteristic of all crystallized substances, built up of well-defined molecules, that structurally equivalent atoms are also chemically identical. It

FIG. 19.—POWDER PHOTO-GRAMS OF AG₃AL, β MANGA-NESE AND CU₅SI. CR-K RAD-IATION.

is true that X-ray analysis has shown that alloy phases have molecular structure only in exceptional cases, but this is the case also with other substances which without doubt may be considered to be chemical compounds—for instance, those formed by ions, as binary salts of the sodium chloride type or by atoms such as $CuAl_2$, Cu_2Mg and other intermetallic compounds. $CuAl_2$ and Cu_2Mg, the atomic grouping of which has been ascertained by J. B. Friauf,[18] have been given as examples because these phases, as shown by the displacement of the X-ray interferences, actually have homogeneity intervals of a certain—though slight—extension.[19] It may, therefore, seem close at hand to assume that in certain cases this difference exists only as to the degree, and that no fundamental difference prevails between phases with extended and phases with narrow homogeneity ranges. It is thus possible, at least in certain cases, that within a large homogeneity interval a fundamental importance may be ascribed to some special
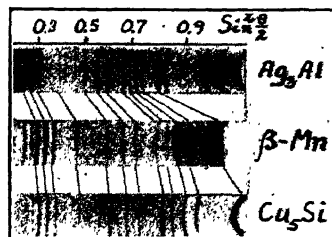
[17] A. Westgren and G. Phragmén: *Phil. Mag.* [6] (1925) **50**, 331.

[18] J. B. Friauf: *Jnl.* Amer. Chem. Soc. (1927) **49**, 3107.

[19] A. Runqvist, H. Arnfelt and A. Westgren: *Ztsch. f. anorg. u. allge. Chem.* (1928) **175**, 43.

concentration, just as in the two cases $CuAl_2$ and Cu_2Mg. It is then justifiable to assume as a definition of this concentration that each group of structurally equivalent points in the crystal lattice at this composition holds only one kind of atoms. On the basis of this conception A. J. Bradley and J. Thewlis found, when determining the atomic grouping of γ brass, that the formula Cu_5Zn_8 should be ascribed to this phase[20] and Bradley has in the same way stated that the corresponding phase in the Cu-Al system should be Cu_9Al_4.[21]

Without doubt this view is quite justifiable with respect to many alloy phases. It is, however, not permissible in a general way to define solid chemical compounds as substances in which structurally equivalent atoms are chemically identical. As a matter of fact, intermetallic phases occur which do not fulfill this condition but which according to conventional ideas certainly must still be looked upon as chemical compounds. Ag_3Al is a substance of this kind. As far as we have been able to determine—even by means of X-ray analysis—it is homogeneous only at a composition exactly corresponding to the formula Ag_3Al; i. e., the components enter in constant and simple stoichiometric proportions.[22]

As may be seen in Fig. 19, the powder photogram of Ag_3Al is almost identical to the one obtained from β manganese. The lattice is cubic and the unit cell contains 20 atoms. According to G. D. Preston, these are, in the case of manganese, divided into two groups, one of 12 and another of 8 structurally equivalent atoms.[23] As the photograms of Ag_3Al and β manganese agree completely as to the relative intensity of the lines, the atomic grouping of these substances must be quite the same. The elementary cube of the silver-aluminum alloy must also contain groups of 12 and 8 structurally equivalent building stones, consisting of silver and aluminum atoms distributed at random. The simple stoichiometric proportions of the Ag-Al phase are thus not due to any crystallogeometrical circumstances but have some other cause. The stability of the atomic grouping probably must be referred to the fact that at the concentration in question the ratio of the number of valency electrons to the number of atoms in the lattice is $3:2$. As a matter of fact, Ag_3Al and Cu_5Si have been found to have β manganese structure. A photogram of the latter phase is also given in Fig. 19; it stands in full agreement with the X-ray photogram of β manganese.

Several investigators engaged in alloy research have expressed the opinion that the question concerning the real character of metallic chemical compounds and solid solutions is of great importance for understanding and fully explaining the equilibrium diagrams of alloys.[24]

[20] A. J. Bradley and J. Thewlis: *Proc. Roy. Soc.* (1926) A **112**, 678.
[21] A. J. Bradley: *Phil. Mag.* [7] (1928) **6**, 878.
[22] A. F. Westgren and A. J. Bradley: *Phil. Mag.* [7] (1928) **6**, 280.
[23] G. D. Preston: *Phil. Mag.* [7] (1928) **5**, 1207.
[24] See, for instance, W. Rosenhain: *Jnl.* Inst. Metals (1929) **42**, 55.

It may be questioned, however, whether this standpoint is valid. As a matter of fact, it appears as though it were scarcely possible to bring about a rational classification of alloy phases by means of the conception chemical compound and solid solution. It does not appear necessary, either. Since X-ray methods have afforded a means of establishing the atomic grouping of these substances, we have obtained a far deeper insight into their chemical character than any classification based on definitions obtained from other parts of chemistry is able to provide.

STRUCTURE ANALOGIES OF ALLOY SYSTEMS

An alloy phase is characterized by its crystal lattice. If this principle is taken as a basis for classifying compound metallic substances a survey is obtained which enables us to trace certain relations between the different alloy systems. Some structure types have been found to recur in several alloys.

Thus, the lattice of γ brass has been encountered in about 20 cases. Phases of this so-called γ type occur in combinations of Cu, Ag and Au with Zn, Cd and Hg (with the single exception of the Au-Hg alloys), in the systems Cu-Al and Cu-Sn and in alloys of Fe, Co, Ni, Rh, Pd and Pt with Zn and in the system Ni-Cd. All these phases excepting γ Cu-Hg contain in their homogeneity range a concentration in which the ratio of the number of valency electrons to the number of atoms is 21:13. We have already given the formulas for a few phases of this kind; i. e., Cu_5Zn_8 and Cu_9Al_4. The representative of this kind of structure which occurs in the bronze system is homogeneous at a composition corresponding to $Cu_{31}Sn_8$. These three formulas agree as to the ratio given above[25] of the number of valency electrons to the number of atoms i. e., 21:13. The γ phases which occur when transition elements Fe, Co, Ni, Rh, Pd or Pt are alloyed with Zn and in the system Ni-Cd are homogeneous at a composition corresponding to formulas of the type Fe_5Zn_{21} and Ni_5Cd_{21}. Here also the ratio of the number of valency electrons to the atom number is 21:13, if the transition elements are looked upon as zero-valent.[25]

A similar law also seems to apply for the phases which, as to structure, are analogous to β brass. Even before β Cu-Al and β Cu-Sn had been analyzed by X-rays, W. Hume-Rothery indicated the possibility that they possessed the same lattice as β brass.[26] This has since been corroborated.[27] The circumstance that the formulas CuZn, Cu_3Al and Cu_5Sn

[25] See footnote 5.

[26] W. Hume-Rothery: *Jnl.* Inst. Metals (1926) **35**, 295.

[27] A. Westgren and G. Phragmén: *Ztsch. f. Metallkunde* (1926) **18**, 279; (1930) **22**, 368; *Metallwirtschaft* (1928) **7**, 700; (1930) **9**, 1919; *Trans.* Faraday Soc. (1929) **25**, 379.

could be ascribed to the three phases caused Hume-Rothery likewise to raise the hypothesis that the stability of these phases depends on the agreement in the ratio 3:2 of the number of valency electrons to the number of atoms. This hypothesis has since been found to hold true in a great number of phases of the β brass type. In this group may also be included FeAl, CoAl, NiAl and possibly also MnAl—in any case at least (Cu, Mn) Al—and here also the valency number per atom is 3:2, provided Fe, Co, Ni and Mn are taken as having a valency of zero.

In certain cases when according to the rule of Hume-Rothery a phase of the β brass type would have been expected, a crystal species with β manganese lattice has been found instead, as already hinted in the foregoing. Just as manganese in the element series V, Cr, Mn and α Fe differs with regard to crystal structure from its neighbors, which all have body-centered cubic lattices, Ag_3Al, Au_3Al and Cu_5Si also differ from Cu_3Al and Cu_5Sn. A phase which has the complicated structure of β manganese has also been detected in the Co-Zn system; its composition appears to correspond to $CoZn_3$. If Co is looked upon as being zero-valent, the valency electron concentration of this phase will be 3:2 here also.

Phases of the close-packed hexagonal lattice type, ϵ, have as a rule fairly wide homogeneity ranges and it has recently been established that their occurrence in alloy systems is of a somewhat more irregular nature than that of the β and γ phases. Within certain alloy series, such as Ag-Zn, Ag-Al, Ag-Sn and Ag-Sb, the homogeneity range of the ϵ phase is, however, displaced—as it appears—in a regular way towards the silver side of the diagrams, in accordance with the increase in valency of the element alloyed with the silver.

Also other structure types besides those occurring in the brass system have been found to appear frequently in the alloy systems. Many metallic phases thus crystallize in the same way as nickel arsenide. V. M. Goldschmidt has shown[28] that they have the following in common: they are built up partly by a so-called transition element—*i. e.* a metal of which the atoms have incomplete inner electron shells—and partly by elements with large and easily polarized atoms such as S, Se, Te, As, Sb, Bi and Sn.

It would carry us too far to render here a full account of all structure analogies hitherto detected in alloy systems. Those cited may suffice to show that the classifying of alloy phases according to their respective structure types has already in many cases proved enlightening with respect to their conditions of formation. Naturally, we are still far from the goal, which is to be able to state, in all cases, the cause of the formation of an alloy phase. As we know, in many alloys crystal species occur

[28] V. M. Goldschmidt: *Chem. Ber.* (1927) **60**, 1286.

which do not seem to have any parallel in other systems. The formation of such special phases evidently depends on special conditions which can scarcely be stated until a more complete theory has been worked out for the relation between lattice equilibrium and atomic properties.

The knowledge regarding a certain relationship between the structure of metallic phases and their atomic properties is naturally of great importance for X-ray research on the constitution of alloys. In the cases in which photograms proving the existence of a crystal lattice of a known and often recurring type are at hand, this is often sufficient for drawing conclusions as to the composition of the phase in question. As evidenced by the above-mentioned analysis of the Heusler alloys, carried out by Persson, this is especially useful for investigating systems which are built up of more than two components. X-ray analysis will also certainly soon be acknowledged as an almost indispensable means of solving the often intricate questions regarding the constituents of ternary—or more complicated—systems.

The likelihood that X-ray analysis may be applied with advantage even for determining the composition of phases in binary alloys in cases where other expedients have proved unsuccessful is evidenced by the following example. Iron-tin alloys belong to the complicated metal combinations which, within a certain concentration interval, divide themselves into two layers while solidifying. Thermal analysis and microscopic methods are therefore hardly applicable here. This is probably the main reason why the above mentioned investigation of these alloys by Wever has led to an incomplete and in certain respects faulty diagram for the Fe-Sn system. In photograms of an Fe-Sn alloy containing about 40 per cent. Sn and quenched from 800° C., Ehret has obtained on the one hand the interferences of α iron and on the other hand a line series which shows that the alloy at this temperature contains a phase with NiAs structure. The iron concentration of this phase consequently may be estimated at about 50 atomic per cent.

CONCLUSION

The X-ray methods are at present only about 15 years old. Naturally, much remains to be done before they can be considered as experimentally completely worked out. The development along experimental lines is proceeding rapidly. Already the X-ray analysis provides an insight into the structure of alloys which was unattainable by the earlier metallographic methods. By means of X-ray analysis the grouping of the atoms of alloy phases may be determined. This new research method is therefore far superior to the older expedients of metallography as a means of establishing the real character of these substances, the chemical nature of which has always been difficult to define. X-ray analysis,

however, is also valuable as a means of solving the primary problem to which investigators in the field of alloy research have devoted themselves with keen interest in recent times; *i. e.* to establish in detail the equilibrium conditions of alloy systems.   The X-ray methods should therefore be applied in the metallographic research institutes as a tool that is at least equal in importance to the older methods.

So far, only a comparatively small part of the vast amount of material represented by metallic systems has been subjected to X-ray investigation.   The results are too meager to allow more than a glance beneath the veil hiding the secrets of the intermetallic reaction conditions.   The part of chemistry that embraces the compound metallic substances therefore still retains, on the whole, the character of uncultivated ground. Our knowledge is still very incomplete regarding the laws that govern the uniting of metal atoms into compound phases.   We may, however, hope that even if a complete solution be unattainable a continued X-ray investigation of alloy systems will eventually provide a much deepened knowledge regarding these problems.   Work of this kind is being carried on in so many places and by so many investigators that the end sought cannot be very far off.

Suppressed Constitutional Changes in Alloys*

By G. Sachs,† Frankfort A/M, Germany

X-RAY analysis and single-crystal study have been utilized in recent years as a new means of following constitutional changes in alloys. If such transformations can be suppressed by rapid cooling, they can be followed at room temperature in a particularly convenient manner. In the following we shall consider changes in solubility and polymorphic transformations with particular reference to phenomena of the age-hardening type. Finally a thermodynamic viewpoint is developed for examining such transformations.

Changes in Solubility

1. Determinations of solubility limits in the solid state which show decreasing solubility with falling temperature are made as follows: A series of alloys extending into the heterogeneous region is prepared and quenched from as high a temperature as possible, whereupon their lattice parameters are determined. Then one or more alloys are quenched from temperatures at which they are heterogeneous and their lattice parameters likewise determined.

For the purpose of determining the parameter the apparatus shown in Fig. 1 has been very useful for it produces sharp films in a short time which can be accurately read. High-order reflections (interferences) from the object are recorded on a film which is placed exactly perpendicular to the X-ray beam. The specimen usually has the shape of a small round bar.[1]

Fig. 2 shows a selection of such exposures of silver-rich Cu-Ag alloys, and Fig. 3 gives the measurements made from these films. Fig. 4 gives the solubility curve which results.[2] This curve is shifted to lower concentrations than the curve that is obtained from metallographic or physical methods. The X-ray method unquestionably gives more reliable data

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* Translated by Samuel L. Hoyt.
† Director of the Metallurgical Laboratory, The Metallgesellschaft A. G. Formerly Divisional Director in the Kaiser Wilhelm Institut für Metallforschung, Berlin, Dahlem.
[1] G. Sachs and J. Weerts: *Ztsch. f. Physik* (1930) **60**, 481–90.
[2] N. Ageew and G. Sachs: *Ztsch. f. Physik* (1930) **63**, 293–303.

than other methods, for it alone gives evidence on the concentration of the solid solution, while it also permits the use of marked supersaturations by means of which equilibrium conditions can be established more rapidly.

2. If a quenched solid solution lies outside the saturation limit at a low temperature, this condition of supersaturation tends to disappear on annealing at a sufficiently high temperature. With this, marked changes in properties are coupled and particularly in mechanical properties which may show quite extreme values. This precipitation process can proceed in two different ways.

FIG. 1.—APPARATUS FOR DETERMINING PARAMETER.

The change in the lattice constants may be gradual with marked diffuseness on one side of the reflections, as has been observed for the aluminum-rich Cu-Al alloys[3] (Fig. 5). The diffuseness is held to be due primarily to lack of homogeneity during the breakdown. During and after the breakdown, however, the crystal lattice remains essentially preserved, according to Fig. 5, even though disturbances in the behavior of single crystals in tensile tests have been observed as a consequence of precipitation.

[3] V. Goeler and G. Sachs: *Metallwirtschaft* (1929) **8**, 671–80.

Secondly, the change to the stable condition may be sudden, as in the silver-rich and copper-rich Cu-Ag alloys, which is shown[4] in Fig. 6. The reflections from the supersaturated portion remain unchanged, showing
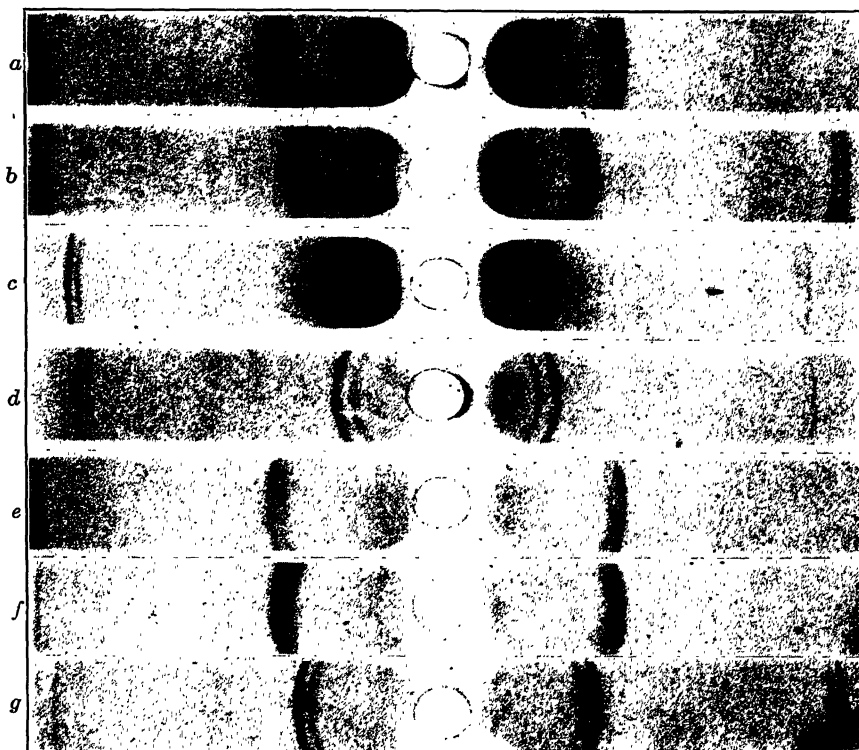

FIG. 2.—PRECISION X-RAY DIFFRACTION PATTERNS OF CU-AG ALLOYS AFTER VARIOUS HEAT TREATMENTS.

    a. Silver.
    b. 7.0 atomic per cent. copper. Quenched from 770° C.
    c. 12.1 atomic per cent. copper. Quenched from 770° C.
    d. 17.3 atomic per cent. copper. Quenched from 770° C.
    e. 10.2 atomic per cent. copper. Annealed 160 hr. at 200° C.
    f. 10.2 atomic per cent. copper. Annealed   5 hr. at 400° C.
    g. 17.3 atomic per cent. copper. Annealed   5 hr. at 600° C.

the lattice to be undisturbed, but those from the stable portion are markedly distorted. The latter shows the lattice to be disturbed but in a manner which has not as yet been explained. In this process the crystal is shown by Fig. 6 to decompose into a disarranged complex.

[4] N. Ageew, M. Hansen and G. Sachs: *Ztsch. f. Physik* (1930) **66**, 350–76.

TRANSFORMATIONS

The mechanism of a transformation in an alloy can be considered as composed of two processes: (1) a rearrangement of the crystal symmetry; (2) a change in the atomic arrangement.
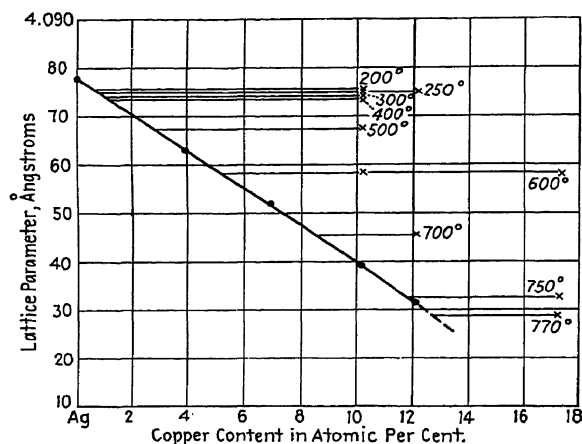

FIG. 3.—LATTICE CONSTANTS OF CU-AG ALLOYS.

1. The AuCu transformation in single crystals has shown that these two processes are at least partly independent of each other.[5] By slow cooling, the cubic solid solution which is stable at high temperatures
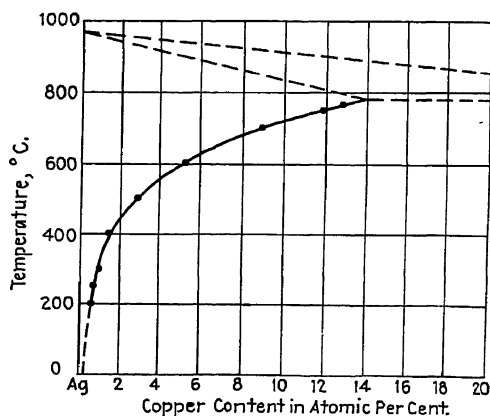

FIG. 4.—SOLUBILITY OF COPPER IN SILVER.

(Fig. 7a) can be transformed with parallel orientation into an almost perfect tetragonal crystal of the "compound," which is stable at low

[5] M. Ohshima and G. Sachs: Ztsch. f. Physik (1930) 63, 210–23.

temperatures (Fig. 7b). The atoms which were statistically distributed (or randomly arranged) in the solid solution have now become regularly distributed.[6] This gives rise to a number of new, so-called "superstruc-
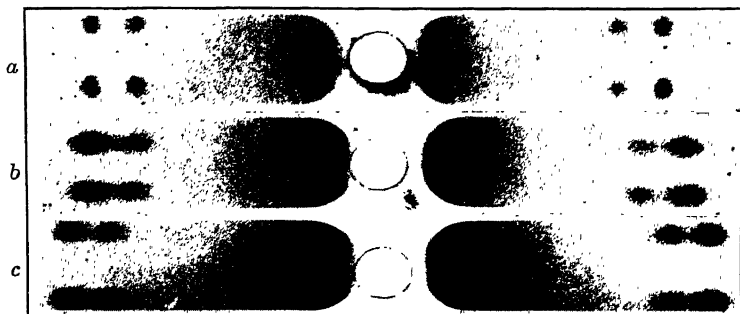

FIG. 5.—PRECISION X-RAY DIFFRACTION PATTERNS OF A CU-AL CRYSTAL WITH 5 WT. PER CENT. COPPER AFTER VARIOUS HEAT TREATMENTS.
a. Quenched at 525° C.
b. Reheated 30 min. at 250° C.
c. Reheated 45 min. at 275° C.

FIG. 6.—PRECISION X-RAY DIFFRACTION PATTERNS OF A CU-AG CRYSTAL WITH 6.3 WT-PER CENT. COPPER, QUENCHED AND REHEATED.
a. Quenched at 800° C.
b. Reheated 20 min. at 250° C.
c. Reheated 40 min. at 250° C.
d. Reheated 20 hr. at 250° C.

tural" reflections in Fig. 7b as compared to Fig. 7a. By more rapid cooling the crystal again becomes tetragonal but the superstructural

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[6] C. H. Johansson and J. O. Linde: *Ann. d. Phys.* (1925) **78**, 439–60; (1927) **82**, 449–78.

lines show an abnormal intensity distribution, according to Fig. 7c. Only the first (001) shows up strongly while the second one is lacking. This shows that the new atomic arrangement has been only incompletely established, in spite of the rearrangement of the lattice, but in a manner which is not yet fully explained.[7]
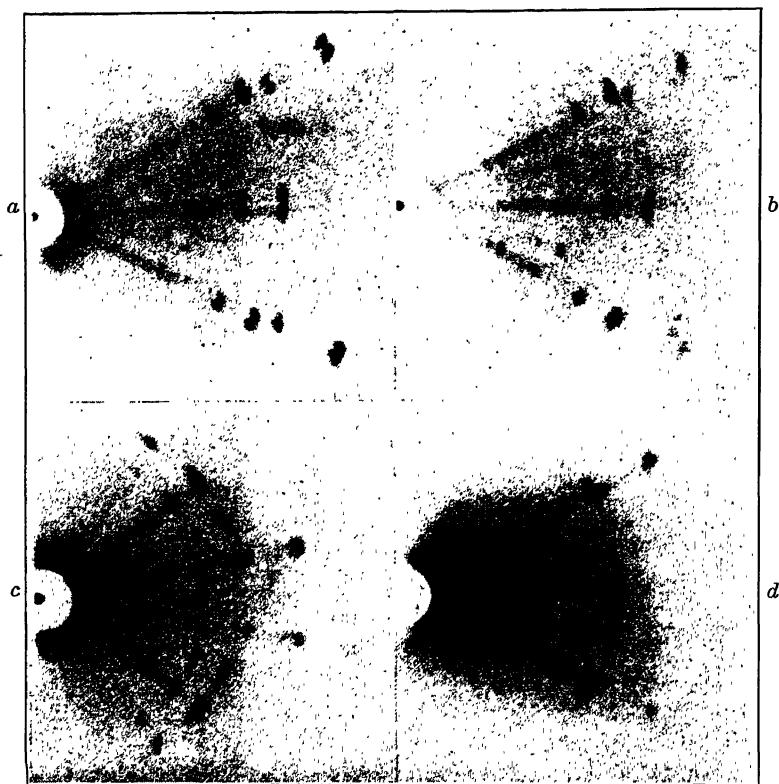

FIG. 7.—ROTATION PATTERNS OF U-CU CRYSTALS AFTER VARIOUS TREATMENTS.
    a. Cubic.   Quenched from 600° C.
    b. Tetragonal.   Cooled very slowly.
    c. Tetragonal.   Accelerated cooling.
    d. Tetragonal.   Quenched and reheated 1½ hr. at 250° C.

2. On annealing the quenched cubic AuCu crystal, the tetragonal lattice results as shown in Fig. 7d with uniformly weak superstructural reflections. This points to an incomplete arrangement of the atoms in the change from solid solution to compound. Upon further annealing the superstructural reflections attain their full intensity with time. The

[7] U. Dehlinger and L. Graf: *Ztsch f. Physik* (1930) **64,** 359-77.

establishment of the final positions follows gradually through all the degrees of disarrangement.

3. In quenched carbon steel there is a body-centered tetragonal structure which is assumed to be an unstable intermediate form in the transformation from face-centered austenite to body-centered alpha iron. The lattice change is practically complete but the carbon, as yet, has failed to precipitate out. Here again the rearrangement of the atoms is more sluggish than the change in crystal form.
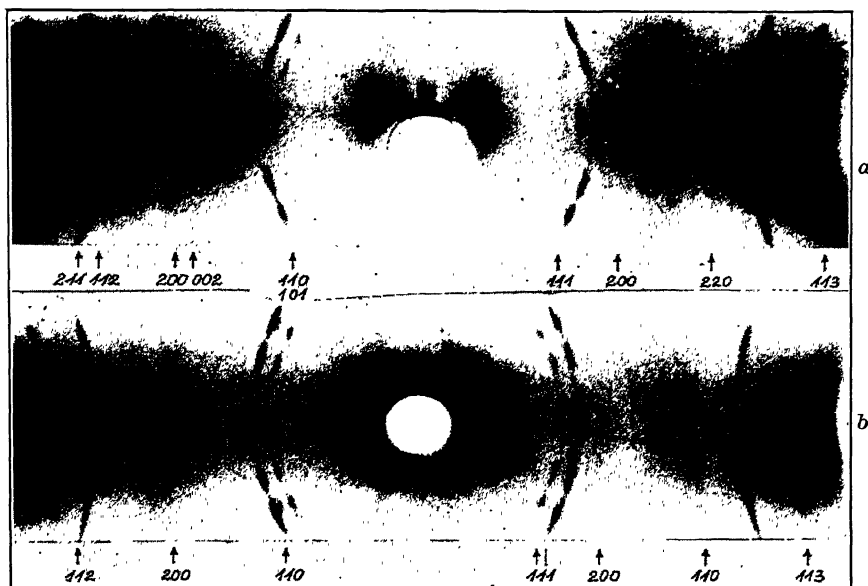

FIG. 8.—ROTATION PATTERNS OF A SINGLE CRYSTAL OF AUSTENITE, PARTLY DECOM-
POSED INTO MARTENSITE.
a. Rotation pattern of "hardened crystal" about cube edge of austenite.
b. Gradual change into stable body-centered cubic lattice of alpha iron.

The tetragonal phase has been shown by examination of a quenched austenite crystal to be oriented in a fixed manner with reference to the parent austenite crystal.[8] Fig. 8a shows the rotation pattern of such a "hardened crystal" about a cube edge of the austenite. The orientation, as determined with the aid of "surface polar figures," shows that the octahedral plane (111) of the austenite is parallel to a rhombic-dodeca-hedral plane (011) of the tetragonal phase and that a face diagonal of the austenite [10$\bar{1}$] is parallel to a body diagonal of the tetragonal phase [11$\bar{1}$]. There are 24 such positions in an austenite crystal.

[8] G. Kurdjumow and G. Sachs: Ztsch. f. Physik (1930) 64, 325–43.

This relationship can be visualized as arising from a combination of the "simple shift" (*einfache Schiebung*) and minor lattice distortions. This is in line with the discontinuous character of the transformation and the fact that it is strongly affected by external forces.
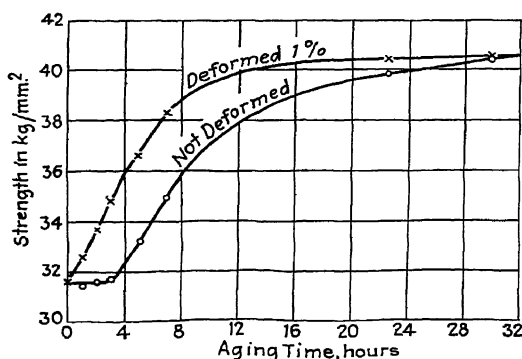

FIG. 9.—EFFECT OF DEFORMATION BY 1 PER CENT. ON AGE-HARDENING OF DURALUMIN (SCHMID AND WASSERMANN).

If the tetragonal lattice is tempered at temperatures of 100°, and above, it changes gradually into the stable body-centered cubic lattice of alpha iron, as is shown by Fig. 8b. This can occur only with the precipitation of carbon out of the lattice, even though the existence of
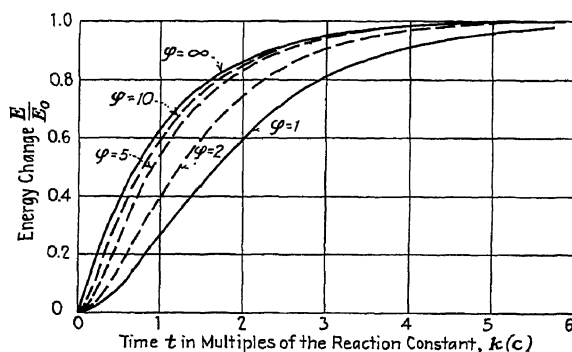

FIG. 10.—KINETICS OF CONSTITUTIONAL CHANGES.

carbon or Fe_3C cannot yet be shown. It is clear from Fig. 8b that the relationship in orientation described above is essentially retained here. Further, it could be shown that this lattice change is fairly sudden and that intermediate concentrations (of carbon in alpha iron) exist only to a minor degree.

KINETICS OF TRANSFORMATIONS

The results discussed above show that transformations in alloys do not all follow one general law, while the picture becomes even more complicated if we select some property and follow its change with time. This is particularly true if, as is frequently the case, the transformation remains dormant for a certain period before commencing, and further that this incubation period can be eliminated by small mechanical deformations (Fig. 9). Furthermore, with copper-aluminum alloys the change in properties occurs far in advance of the precipitation while with the copper-silver alloys the two effects occur simultaneously.

A conception which is capable of throwing light on such behavior can be developed as follows: Instead of considering this as a constitutional change, we may consider it more broadly as an energy change. Such an energy change may be considered as consisting of two steps: (1) the activation of the material with a definite activation velocity, (2) the change in the specific energy of each activated particle with a definite rate of change.

Here we shall limit the calculation to the simplest case in which the amount activated in unit time is proportional to the amount that has not been activated $(M_0 - M)$:

$$dM = c(M_0 - M) \cdot dt \qquad [1]$$

and the change in specific energy per unit time is proportional to the excess energy at that time:

$$-d\epsilon = k \cdot \epsilon \cdot dt \qquad [2]$$

c and k are the material constants which control the two processes.

Integrating equation 1 gives

$$\frac{M_0 - M}{M_0} = e^{-ct}$$

and

$$dM = cM_0 \cdot e^{-ct} \cdot dt \qquad [3]$$

From equation 2

$$\frac{\epsilon}{\epsilon_0} = e^{-kt} \qquad [4]$$

$$d\epsilon = -k \cdot \epsilon_0 \cdot e^{-kt} \cdot dt \qquad [5]$$

The energy of the amount of material activated in time t to time t', dM, is then:

$$dE = dM\left(\epsilon_0 - \int^{t'} \cdot d\epsilon\right)$$

$$= dM\epsilon_0[1 - e^{-k(t'-t)}] \qquad [6]$$

and the energy at that time is, from equation 3,

$$E = \int_0^{t'} dM \cdot \epsilon_0 [1 - e^{-k(t'-t)}]$$

$$= \int_0^{t'} M_0 \cdot e^{-ct} \cdot \epsilon_0 [1 - e^{-k(t'-t)}] dt$$

$$= M_0 \epsilon_0 \int_0^{t'} [c \cdot e^{-ct} - c \cdot e^{-(c-k)t - kt'}] dt$$

and with $M_0 \cdot \epsilon_0 = E_0$ and $c/k = \phi$, we get finally:

$$\frac{E}{E_0} = 1 + \frac{1}{\phi - 1} \cdot e^{-\phi k t'} - \frac{\phi}{\phi - 1} e^{-kt'} \qquad [7]$$

According to these equations, the change in energy with time depends on the ratio of the two reaction constants c and k. If $\phi = 0$, when $k = \infty$, the law becomes that of radioactive decay and the energy change follows the logarithmic curve. The same law is observed when $\phi = \infty$, i.e., $c = \infty$. These two cases are differentiated from each other in that the energy distribution will differ. As ϕ increases up to $\phi = 1$, the incubation period becomes more prominent, as is shown in Fig. 10. Its disappearance on straining can be said to be due to a marked increase in the activation velocity with but a minor change in the energy factor.

The law governing transformations which is developed here leads to a better understanding of the incubation period and its disappearance. Quantitatively observed, incubation times are often much greater than the maximum value given by equation 1. Even this can be reached if we modify the activation law so that the speed of activation increases with time.

DISCUSSION

(C. H. Mathewson presiding)

C. S. SMITH, Waterbury, Conn.—I would like to raise a minor point which perhaps does not strictly belong to the discussion of this paper. We are accustomed to hearing of X-ray methods a sideal and supplanting older methods. For instance, on page 39 we find the statement, "The X-ray method unquestionably gives more reliable data (in determining solubility limits) than other methods," etc. The X-ray method is undoubtedly useful in determining the solubility limits at low temperatures, particularly in the neighborhood of room temperatures, where it is superior to other methods. Its great sensitivity permits the detection of a constituent in particles of a size smaller than the limit of microscopic resolution and the detection of a change in lattice parameter due to concentration changes undetectable by the microscope. Its sensitivity is, however, a disadvantage when dealing with samples quenched from high temperatures. As long as the exposure is made actually at the temperature at which the reaction is being studied the method is free from objection, but frequently diffraction patterns are obtained on samples quenched from a high temperature and exposed at room temperatures. This method almost invariably shows less solubility than the microscope indicates, yet it is the higher limit determined by the microscope which is more likely to be correct, for the diffraction pattern is that of the solution

which may have been partly decomposed during cooling. Just as it is obviously impossible to determine the temperature limits of gamma iron from diffraction patterns of quenched samples, in many cases it is equally difficult to prevent some changes in the concentration of a quenched alloy, particularly when the boundary is steeply sloped, and the diffraction pattern will be that of an alloy in an undeterminable intermediate condition. If a sample has been annealed for a sufficiently long time to enable equilibrium to be reached, a prerequisite for any method of examination, the minor constituent will always have grown to appreciable size, owing to diffusion, and it will be possible to identify it easily under the microscope, even if it has partly or completely decomposed during quenching. Changes in the solid solution matrix will usually be invisible under the microscope, but even if the rate of cooling is sufficiently low to permit visible precipitation, the precipitated particles can generally be distinguished. The diffraction method will show only the phases actually present, and it does not permit allowance for decomposition. This objection to the method is so frequently overlooked that some emphasis seems desirable.

R. S. DEAN, Washington, D. C.—A study of a number of dispersion-hardenable alloys indicates a behavior similar to that described by the author; namely, the existence of an incubation period before the hardening takes place. The question of what takes place during this period is a most interesting one. Very likely it is a period of formation of nuclei around which the separating phase eventually forms. But what is the nature of these nuclei? On this point I would like to introduce an interesting bit of evidence. If a lead-calcium alloy containing 0.08 per cent. calcium is quenched and held for 1 hr. at a given temperature and then heated at a series of temperatures, the heating temperature at which maximum hardness is obtained depends on the temperature at which it has been held for 1 hr.; the higher this "incubating" temperature, the higher will be the temperature at which the maximum hardness will be observed.

This indicates that the temperature of softening is dependent on the temperature at which the nuclei are formed, and that the rise and fall of hardness is in essence the formation and decomposition of these nuclei, the only other essential being sufficient mobility in the lattice so that the atomic arrangement may conform to the nuclei.

A similar phenomenon has been observed in hardening copper wire by cold work. If wire is drawn at elevated temperatures but below the annealing temperature, its annealing temperature is increased. In other words, it appears that the way to breed heat-resistant nuclei is at high temperature.

In 1927, Mr. Gregg and I suggested[9] that hardening was due to the formation of what we termed "pseudomolecules" which might have varying energies and hence temperatures of decomposition. I believe this hypothesis will be useful in studying incubation periods.

YAP, C. P., New York, N. Y.—I agree with Mr. Dean, but I should like to express Dr. Sachs' idea of a period of activation in different words. Much of our work on solid solubility is somewhat invalidated by the fact that the solubility in the solid state is a function of the particle size of the solid solute in equilibrium with the solution. For this reason, I am strongly inclined to doubt the value of extremely refined methods of locating the limits of solid solubility, unless the particle size and surface energy are taken into consideration.

We have the well-known Kelvin-Ostwald-Freundlich equation governing the relation between solubility and particle size, thus:

[9] R. S. Dean and J. L. Gregg: General Theory of Metallic Hardening. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 375.

$$RT \ln \frac{s_2}{s_1} = \frac{2M\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad\qquad [A]$$

in which R, T and M have the usual significance, s_2 and s_1 are the solubilities of the solute of radius r_2 and r_1, σ is the surface energy and ρ the density of the solute. If we let s_1 be the normal solubility, $1/r_1$ becomes negligible compared to $1/r_2$, so that equation A reduces simply to

$$\ln s_2 = \frac{2M\sigma}{RT\rho r_2} + \ln s_1 = \frac{k}{r_2} + \ln s_1 \qquad\qquad [B]$$

It is seen at once that the degree of supersolubility depends essentially upon the value of r, and for every temperature there is an equilibrium particle size. Those particles of radius less than the equilibrium radius are unstable and will grow larger and larger. I call this a "period of nucleation." In a paper almost ready for publication, I have developed these relations at some length.

Z. JEFFRIES, Cleveland, Ohio.—We are much indebted to the authors from across the water for these splendid contributions[10] and we hope that they will submit other manuscripts for future publication. I should like to point out in connection with Dr. Sachs' paper that natural or artificial aging or precipitation hardening cannot be completely explained by a simple assumption of an incubation period; that is, a period of zero activity. In Fig. 9, the aging curve of the undeformed specimen should really have passed through a minimum tensile strength prior to the increase. The fact that the difference appears to be small in this case does not justify the plotting of the curve as a horizontal followed by a rise. As a matter of interest, we have investigated not one but many age-hardening alloys, and we find many cases in which the hardness and strength pass through minimum values during the process of aging.

It is not peculiar to our investigations. It has been reported from Germany, England and Japan, and with other alloys besides the light alloys, so we must consider, at least in many cases, something in the way of a positive softening factor during the early stages of aging. Professor Sauveur's twisting tests made on steel during the transformation from one crystal form to another have a bearing on this point. He found a state of extreme softness and plasticity while the steel was in process of transforming. The material is in a metastable state while an internal change is progressing. The mere deformation incident to the tensile test or hardness determination will have or may have a weakening or softening effect. This phenomenon, however, is not confined to room-temperature aging. Minimum values are found in artificial aging when the subsequent testing is done at room temperature, so that the whole matter becomes complex when an attempt is made to offer anything like a complete interpretation.

I will offer one thought, however, along these lines. If we should determine the properties of a baseball pitcher just after he had delivered the ball we would find his characteristics normal, that is, while the ball was still in the air; but just before the pitcher delivered the ball, he would have exhibited different characteristics.

Many atoms, during aging, are in a state of transition, like the ball in the air. In the process of aging they are trying to reach a state of equilibrium. In the early stages of aging, we may encounter a good many of these atoms in transit in such a manner that the force of diffusion and compound formation actually assist slip movement.

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[10] This refers also to the paper by Dr. Wever, on page 51.

Texture of Metals after Cold Deformation*

By Franz Wever,† Düsseldorf, Germany

According to Tammann,[1] the explanation of the effect of mechanical deformation in producing changes in the properties of metals is one of the most important problems of physical metallurgy, taking rank with the study of the constitution of alloy systems; and this problem has long attracted the attention of practitioner and scientist alike. Its solution was not advanced materially until Tammann[2] set up his translation hypothesis with its crystallographic basis, while other hypotheses, such as the amorphous metal hypothesis of Beilby[3] and Rosenhain,[4] have been shown by more intensive studies to be less and less satisfactory. The principles of the Tammann translation hypothesis have proved to be useful even up to today and in spite of all of the recent accumulation of experimental data, while the differences of opinion which have arisen relate to the extent to which the hypothesis accounts for the observed changes in properties and to what extent further assumptions are necessary.

Stimulated by the proposals of Tammann, there soon developed a lively experimental activity which aimed at the elucidation of the structural or crystallographic changes produced by the mechanical deformation of metals. Parallel movements of crystal "blocks" along definite crystal slip planes had already been observed by Ewing and Rosenhain[5] in 1900, in metals which had been moderately deformed but without shedding light on the crystallographic nature of the processes accompanying more severe deformation. The solution of this important problem was not advanced until a much later date, or until the methods of X-ray crystal analysis had become available. Shortly after the discovery of the diffraction of X-ray by crystals, symmetrical diffraction effects were

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* Translated by Samuel L. Hoyt.

† Kaiser-Wilhelm-Institut für Eisenforschung.

[1] G. Tammann: Lehrbuch der Metallographie, 3. Leipsig, 1914. L. Voss.

[2] G. Tammann: *Op. cit.*, 54.

[3] G. T. Beilby and H. N. Beilby: *Proc.* Roy. Soc. London (1905) A76, 462.

[4] W. Rosenhain: *Int. Ztsch. f. Metallographie* (1914) 5, 65.

[5] J. A. Ewing and W. Rosenhain: *Phil. Trans.* Roy. Soc. London (1900) A193, 353.

observed by Hupka[6] on metal foils, which effects disappeared after the foil was heated. Many similar effects were subsequently observed but without furnishing an explanation. It was not until 1920 that it was shown by Uspinskij and Konobejewski[7] that this diffraction effect of cold-rolled metals was due to a directed arrangement of the crystallites, but this work was not known outside Russia until later. A little later it was found by Becker, Herzog, Jancke and Polanyi[8] that cold-drawn wires gave diffraction patterns similar to those of rolled foils and, in agreement with Uspinskij and Konobejewski, the viewpoint was developed that the quasi-isotropic arrangement of the annealed metal was rearranged by the cold deformation in such a way that the crystallographic axes assumed more or less definite directions in space. The similarity of this statistically anisotropic arrangement to natural fibrous materials led to its designation as "fiber structure."

This important observation gave special significance to the study of crystal structure of cold-worked metals for its statistical anisotropy must be a direct consequence of the mechanism by which plastic deformation proceeds, and therefore it was to be expected that the determination of this structure would lead to a clearer understanding of the inner processes of plastic deformation. On this account many investigations in different countries were taken up which have thoroughly revealed the texture produced by various processes of cold deformation, such as drawing, rolling, pressing, etc. Résumés of these results have been published repeatedly and a reference to them will suffice here.[9]

These investigations, however, gave rise to hopes which have only in part been fulfilled. The arrangements of crystallites in drawn wire and in symmetrically pressed test pieces have been established by various investigators, in good agreement with each other, and their results have seemed to be in close accord with the fine mechanism of the deformation process. The results obtained with cold-rolled foil have been contradictory, so much so as to suggest that the effects were of a much more complex nature than had been supposed. On this account it was not possible to set up a satisfactory hypothesis which could be tied in with the slip mechanism in single crystals.

This lack of agreement can be accounted for on the one hand by the manner in which the tests were conducted and in the description of the results thereof while, on the other hand, the earlier expectations that were entertained were, in part at least, based on false assumptions.

[6] E. Hupka: *Physik. Ztsch.* (1913) **14,** 623.
    Nature (1913) **91,** 267.
    [7] N. Uspinskij and Konobejewski: Lecture before Russian Physical Lebedev Soc., April 30, 1920, Moscow.
    [8] K. Becker, R. O. Herzog, W. Jancke and M. Polanyi: *Ztsch, f. Physik* (1921) **5,** 61.
    [9] See, for example, G. Masing and M. Polanyi: *Ergeb. d. Exakt. Naturwissenschaften* (1923) **2,** 177.

According to the views that guided the course of the earlier investigations, it was anticipated that the crystallites in a severely deformed metal would show only one or a limited number of discreet orientations with rational lattice directions lying in the direction of the major deformations. In a crystallographic sense, this was to be held responsible for the aniso-tropic character of the texture produced. Furthermore, it was expected that this texture would be reproduced in accordance with the symmetry of the deformation process. In accordance with these ideas severely rolled foil was generally used for test and the results were reported by assigning rational lattice directions to the major axes of deformation, with a certain amount of dispersion.

On the other hand, this picture of the situation gives rise to certain doubts. The macroscopic features of the rolling process show that this deformation is definitely heterogeneous in character and that it is subject to influences from the most varied sources. From this it is clear that the texture will vary from point to point and that it may be affected by such factors as the roll diameter, the reduction per pass, the number of passes, etc. Again various observations[10] suggest that the fine mecha-nism of the process varies (or may vary) fundamentally in the course of the reduction.

But, what is of paramount significance here if we wish to get at the crux of the situation, it is to be assumed that certain orientations are actually attained by the crystallites if the deformation process is carried far enough, even though the actual tendency may be otherwise, and thus that these orientations become a part of the final result. In this way the characterization of the final texture by means of ideal orientations may give an incomplete and arbitrary analysis which does not accurately reflect the inner mechanism of the deformation. In this way errors may be committed in deducing the mechanism of the slip process from the final texture produced by that process.

The basis for a study of the relationship between the orientation of the crystallites in a cold-deformed metal and the slip mechanism must be a complete and unprejudiced description of the findings of the X-ray analysis. This can be accomplished by means of "pole figures" as has been done by F. Wever.[11] It is only by means of such a tool that one can attempt to develop the relationships of the texture and, from them, the mechanism of intercrystalline deformation.

The method suggested by Wever for describing the texture of plas-tically deformed metals is the "pole figure" method used in crystallog-raphy to represent crystal symmetry. Each crystal face is represented by the point of intersection of its normal with a circumscribed sphere, its

[10] G. Tammann and A. Heinzel: *Ztsch. f. Metallkunde* (1927) **19**, 338.

[11] F. Wever: *Mitt. K-W. Inst. Eisenforsch.* (1924) **5**, 69; *Ztsch. f. Physik* (1924) **28, 69.**

polar surface; the stereographic projection of the sphere gives the "polar surface figure" from which all of the elements of symmetry can be directly read.   To utilize this well-tried method of the crystallographers for the description of textures, the conception of the crystal face is replaced by the plane of the crystal lattice while, for simplicity, the pole figure of each lattice plane complex (*hkl*) is treated individually.   This method can also be used for polycrystalline materials without alteration, in that we represent the randomly oriented grains by uniformly spaced intercepts of the surface normals ("surface poles") on the sphere.   In this sense a statistically anisotropic structure occupies an intermediate position between the single crystal and the polycrystal structure, for in it definite crystallographical directions of all of its crystal fragments are arranged in more or less parallel directions.   Here the distribution of the polar intercepts contracts into limited surfaces of characteristic shapes.   The shapes of these areas and their locations give a complete and readily visualized characterization of the fiber structure (anisotropy) of the sample under investigation.

This method of representing fiber structures is clarified by the direct relation between the polar surface figures and the X-ray diffraction pat-

FIG. 1.—RELATIONSHIPS OF METHOD OF REFLECTION PROJECTION.

terns.   The latter, according to F. Rinne,[12] reproduces the "reflection projection" of a section through the polar sphere in which each point in the subject P corresponds to a point in the image π which lies in the same plane of incidence with it and is reproduced by reflection from the corresponding plane according to the Bragg reflection angle $\delta/2$. This gives a "reflection circle" after Polanyi,[13] with the angular opening of $90 - \dfrac{\delta}{2}$ around the incident beam whose axis is the geometrical location of the "surface pole," and which is recorded by radiation of the wave length $\lambda = 2d \sin \dfrac{\delta}{2}$.   The simple relationships of the method of "reflection projection" are represented diagrammatically in Fig. 1.   From this the construction of the complete pole figure follows, to wit: The sample is radiated with monochromatic radiation in different directions and in such a way that the reflections produce a sufficiently dense net on the surface

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[12] F. Rinne: Einfuehrung in die kristallogr.   Formen lehre, Ed. 4, 218.   1922.
[13] M. Polanyi: *Ztsch. f. Physik.* (1921) **7**, 149.
   M. Polyani and K. Weissenberg: *Ibid.* (1922) **9**, 123.   *Ibid.* (1922) **10**, 44.

of the sphere, and finally by combining the patterns by means of simple methods of graphical geometry. A camera which was developed for this purpose is shown in Fig. 2. It provides for rotation in two directions so that the sample can be radiated from any direction. An improved
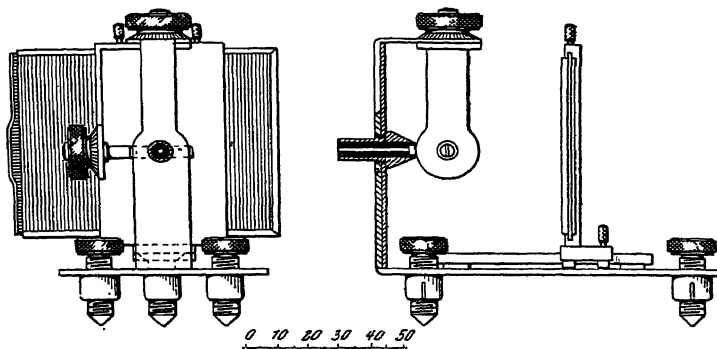

FIG. 2.—FIRST CAMERA DEVELOPED FOR REFLECTION PROJECTION.

form is shown in Fig. 3 which permits a parallel movement of the sample during exposure. The brass frame R, which holds the sample, is movable in the collar H by means of the pin Z. The movement of the sample is produced by the shutter motion and cam E, which is rotated by clock-
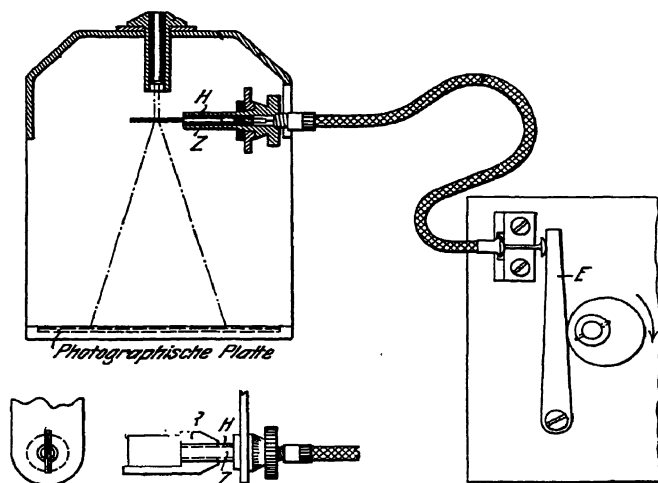
FIG. 3.—IMPROVED CAMERA FOR REFLECTION PROJECTION.

work. This movement of the sample during exposure has the object of increasing the volume radiated and thus to make more certain of securing positive results which give a statistical record of the crystallites which are radiated. This is particularly valuable with relatively coarse-

grained starting materials when the portion in the cross-section of the primary beam is no longer to be considered quasi-isotropic. Furthermore, the effects of the nonuniformly etched structure can be modified.

The geometrical relationships that govern the reproduction of the pole figure from the diffraction patterns have been considered above. It happens, however, that inconveniences in its practical application have hindered a more general use of this method of analysis.
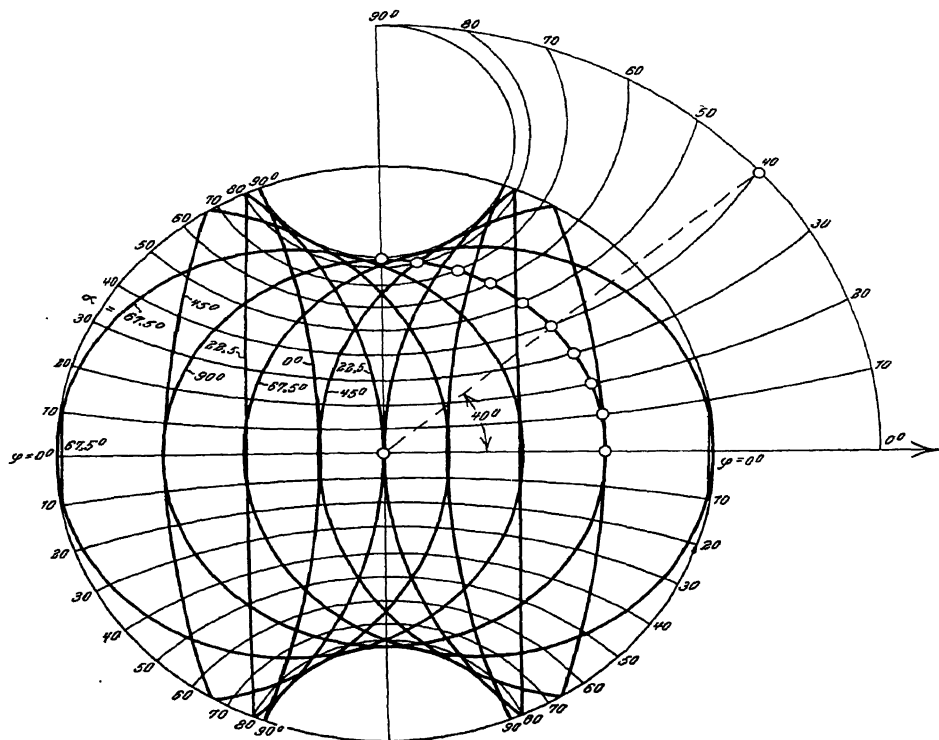

Fig. 4.—Chart for working out diffraction pattern of aluminum with copper radiation for the cube face (001).

A material simplification of the drafting work can be accomplished by means of charts in which the points of a Debeye-Scherrer circle can be directly allocated to the corresponding points of the polar sphere, as has been shown by F. Wever and W. E. Schmid.[14] By this means the spots found on the exposures can be plotted for their planes in the appropriate places of a sterographic projection of the polar sphere. The simple geometrical construction of such charts cannot be given here, but examples are given in Figs. 4 to 6, which reproduce charts for

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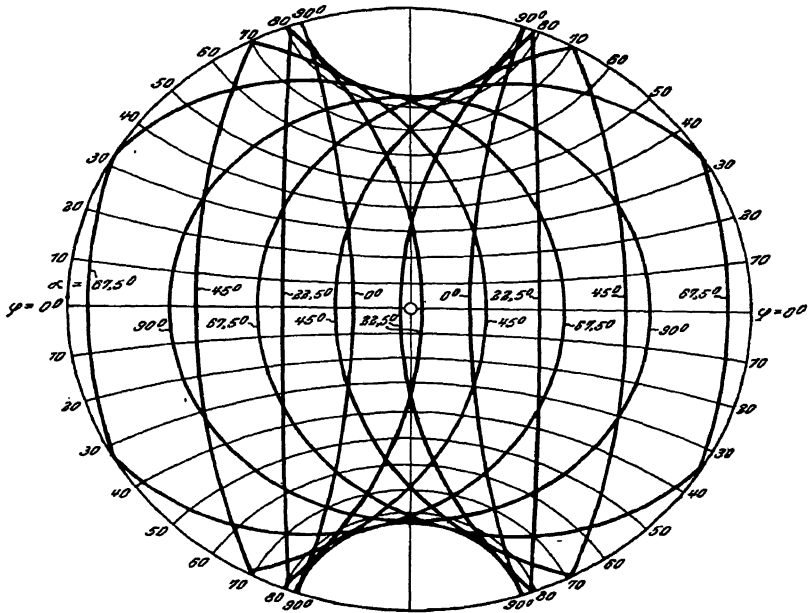[14] F. Wever and W. E. Schmid: *Mitt.* K-W. Inst. Eisenforsch. (1929) **11**, 109.

FIG. 5.—CHART FOR WORKING OUT DIFFRACTION PATTERN OF ALUMINUM WITH COPPER RADIATION FOR THE OCTAHEDRAL PLANE (111).
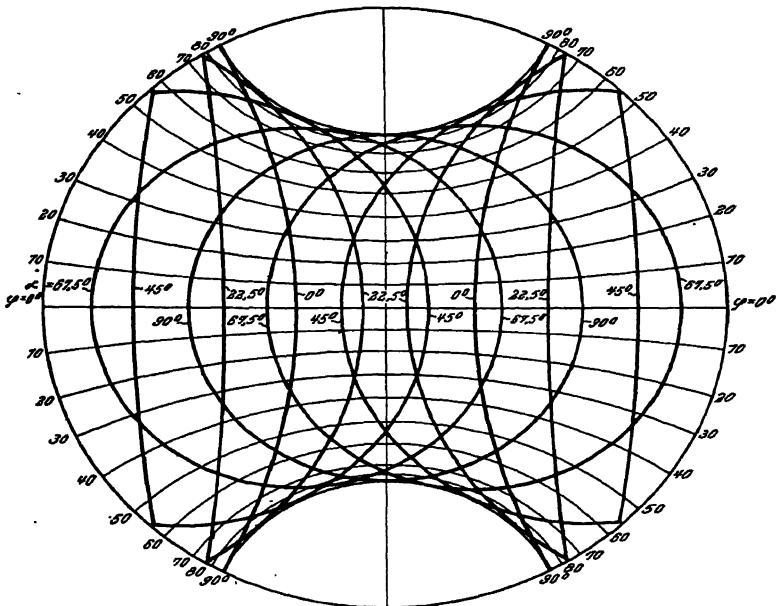

FIG. 6.—CHART FOR WORKING OUT DIFFRACTION PATTERN OF IRON WITH IRON RADIATION FOR THE DODECAHEDRAL PLANE (011).

working out the diffraction patterns of aluminum with copper radiation and iron with iron radiation for the cube face and for the octahedral and dodecahedral planes respectively.

TEXTURE OF COLD-DEFORMED METALS

It is realized that the following discussion of the texture of cold-deformed metals is incomplete in that no attempt is made to give a comprehensive review of previous publications. Furthermore, only a brief résumé will be given of the special case of the cubic metals, which have been most carefully studied, and which confirm the more meager observations on noncubic metals only with respect to the conclusions drawn.
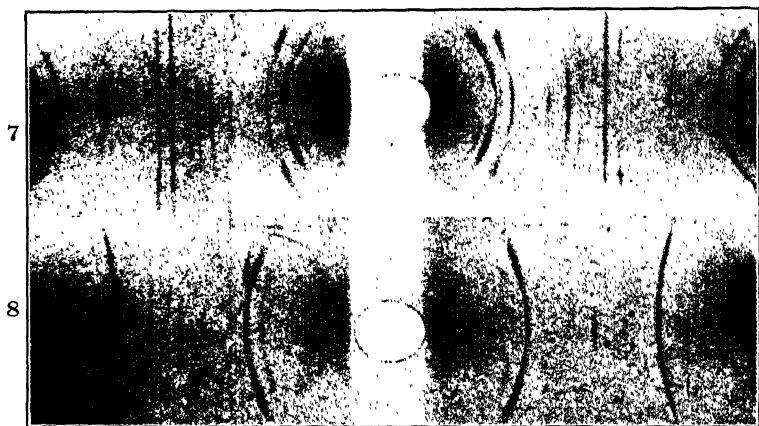

FIG. 7.—DEBEYE-SCHERRER DIAGRAM OF COLD-DRAWN COPPER (FCC).
FIG. 8.—DEBEYE-SCHERRER DIAGRAM OF COLD-DRAWN IRON (BCC).

The numerous studies of the texture of cold-drawn metals should give the crystallographic direction that functions as the direction of slip under the assumption that the rational lattice direction that becomes parallel to the direction of extension is identical with the direction of slip. The result can be clearly summarized for both face-centered and body-centered cubic metals as follows: One of the most densely populated planes assumes a position normal to the direction of pull, while, at the same time, all of the remaining planes of the same type assume symmetrical positions about that direction.

To depict these conditions, the Debeye-Scherrer diagrams of cold-drawn copper (FCC) and of iron (BCC) are reproduced in Figs. 7 and 8. The corresponding locations of the crystal lattices for the densest planes in each case are given in Figs. 9 and 10. F. Koerber[15] has characterized the symmetrical position of the plane of greatest density as that for which

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[15] F. Koerber: *Mitt.* K-W. Inst. Eisenforsch. (1922) **3**, 1.

the shear resistance has attained a maximum value and that any rotation out of that position would result in a decreased shear resistance for at least one of the planes.
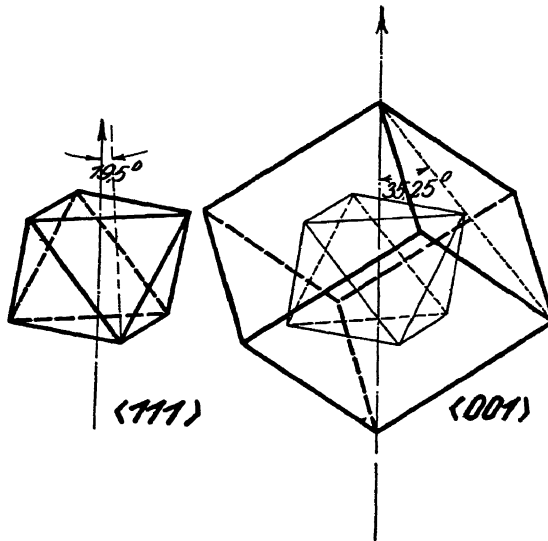

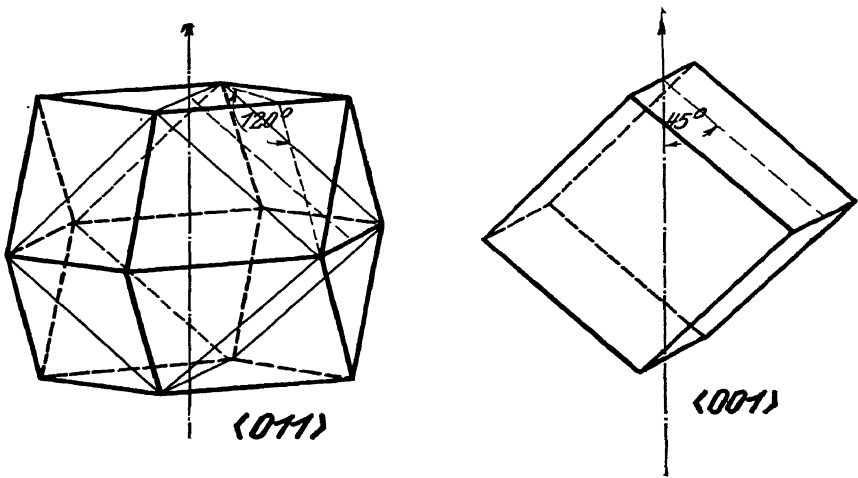FIG. 9.—LOCATION OF CRYSTAL LATTICE FOR DENSEST PLANE OF FIG. 7.

FIG. 10.—LOCATION OF CRYSTAL LATTICE FOR DENSEST PLANE OF FIG. 8.

TEXTURE OF COLD-COMPRESSED METALS

A splendid amplification of these observations, and also a confirmation of the conclusions drawn, on the relation between the texture and

the strengthening effect comes from studies on cold-compressed metals.[16] For this purpose, test bars of copper and iron were compressed by about 80 per cent. by means of the cylindrical compression process described by E. Siebel.[17]   Small test bars were cut out of the axes, and the resulting Debeye-Scherrer patterns are reproduced in Figs. 11 and 12.   The lattice orientations obtained therefrom are given in Figs. 13 and 14.

A correlation of the textures produced by tension and by compression is not directly evident, but it becomes so when one takes into account that it is the symmetry of the direction of flow, rather than the axis of symmetry of the applied stress field, that is of significance.   In drawing, this coincides with the tensile axis (direction of pull), while in compres-
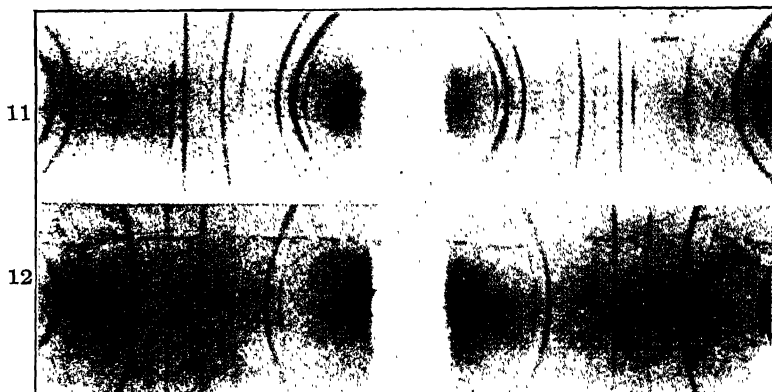

FIG. 11.—DEBEYE-SCHERRER DIAGRAM OF COLD-COMPRESSED COPPER.
FIG. 12.—DEBEYE-SCHERRER DIAGRAM OF COLD-COMPRESSED IRON.

sion it lies in a plane perpendicular to the direction of the compression axis.

The fiber texture produced in face-centered cubic metals by drawing is shown by Fig. 9 to have a plane of densest packing (111) perpendicular to the direction to the flow of the material with the remaining (111) planes symmetrically disposed and inclined to it at an angle of 19.5°. From this it follows that the indices of the tensile axis are (111).   This orientation is reproduced in all its essential details in the texture produced by compression (Fig. 13).   In accordance with the change in the direction of flow, we now have the maximum number, or two 111 directions in the plane of flux which gives two (111) planes perpendicular to this plane. Fig. 10 shows that tensile extension of body-centered cubic metals results in a plane of densest packing, (011) perpendicular to the direction of flow with a 011 direction parallel thereto.   The texture after compression

[16] F. Wever and W. Schmidt: *Ztsch. f. Tech. Phys.* (1927) **8**, 398.
[17] E. Siebel: *Mitt.* K-W. Inst. Eisenforsch. (1927) **9**, 157.

again has the maximum number of the 011 directions in the plane of flux, which is three in this case, with three (011) planes perpendicular thereto.
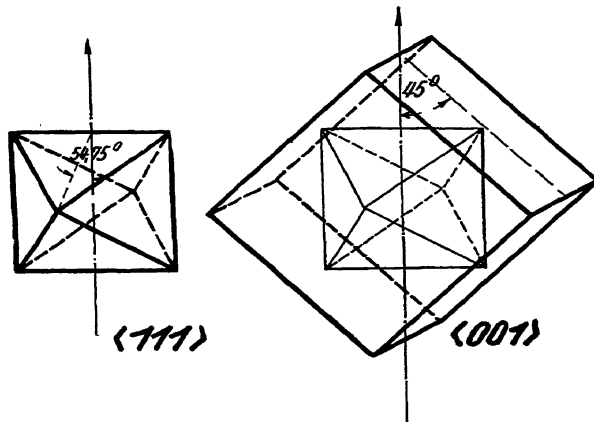

Fig. 13.—Lattice orientation obtained from cold-compressed copper.

The analysis made of the tensile test by Koerber can be directly and logically extended to the compression test. Independent of the method of working, planes of greatest atomic density are always perpendicular to the direction of flow, and it is only the multiplicity of this distribution that is determined by the symmetry properties of the directions of flow.
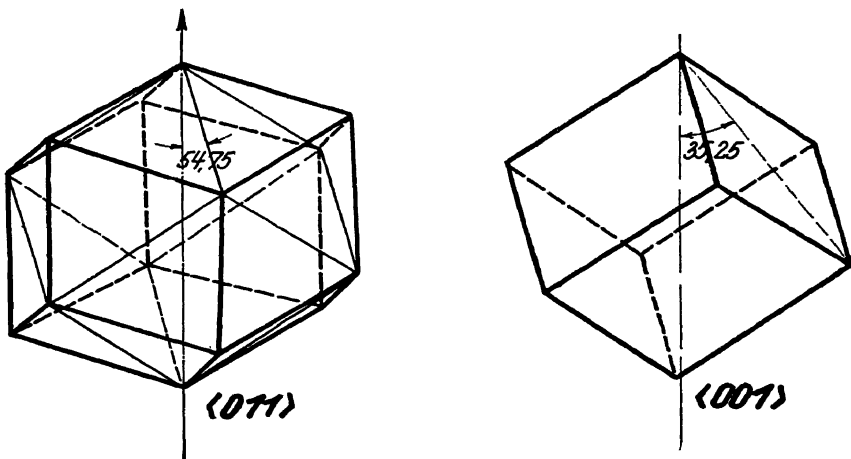

Fig. 14.—Lattice orientation obtained from cold-compressed iron.

In tensile extension this direction coincides with the tensile axis, so that the crystallites are oriented with these planes parallel thereto with the same indices. In compression the direction of flow of the metal is in a

direction perpendicular to the compression axis, which gives a texture that is characterized by the largest number of equivalent planes of the type in question perpendicular to the plane of flow.

TEXTURE OF COLD-ROLLED METALS

The numerous studies of the texture of cold-rolled metals can be subdivided into two groups, as was mentioned at the beginning. With fundamentally similar methods, they utilize different means of representing their results and also differ materially in the results themselves. Following the work of H. Mark, M. Polanyi and K. Weissenberg[18] on fiber diagrams, the first group is limited to a description of the arrangement of the crystallites by giving their ideal, rational indices with reference to the major axis of the deformation process as well as the observed
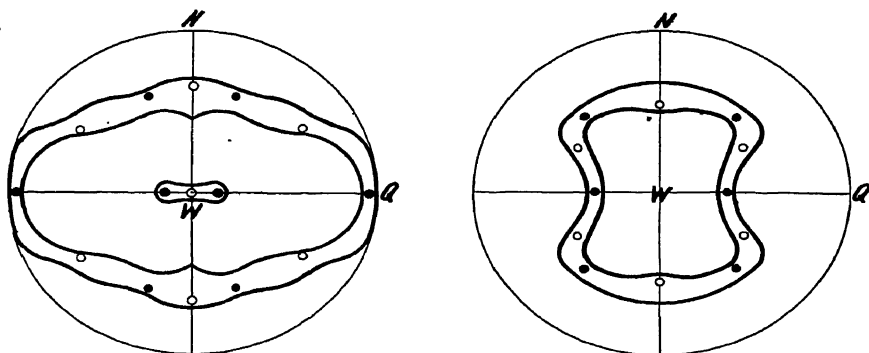

FIG. 15.—POLE FIGURES FOR OCTAHEDRON AND CUBE OF ALUMINUM.

spread of the observed positions with respect to the ideal position.[19] In these works on face-centered cubic metals, the orientation is given by all as a 112 direction parallel to the direction of rolling and the 111 direction parallel to the transverse axis or the (110) plane parallel to the plane of rolling.

A new principle for depicting the results was utilized by F. Wever[20] in 1924 which arose from the realization that a description of the rolling structure by means of the ideal, rational position ultimately arrived at is not capable of bringing out the pertinent relationships. By making use of the methods of crystallographers, complete "pole figures" of the most important planes were set up and only then was the attempt made to analyze them in terms of ideal crystallite positions and the spread. The results of this work of F. Wever differ considerably from those given

[18] M. Polanyi: References of footnote 13.

[19] F. Wever and W. Schmidt: *Ztsch. f. Tech. Phys.* (1927) **8**, 398.
   G. Masing and M. Polanyi: *Op. Cit.*

[20] F. Wever: References of footnote 11.

above and on the basis of rotation patterns it is assumed that the pole figure is primarily determined by a lattice arrangement in which the 111 direction lies in the direction of rolling and the 011 direction in the cross direction. As an example, the pole figures for the octahedron and cube of aluminum are reproduced in Fig. 15. W represents the direction of rolling, while N is the normal and Q the cross direction of the foil.

A systematic search for rational crystal orientations that would be compatible with the pole figures and satisfy the conditions of symmetry of the deformation process led to the finding that only those positions which Mark and Weissenberg and Wever had assumed satisfy these
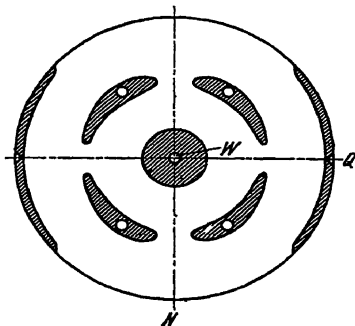

FIG. 16.   FIG. 17.

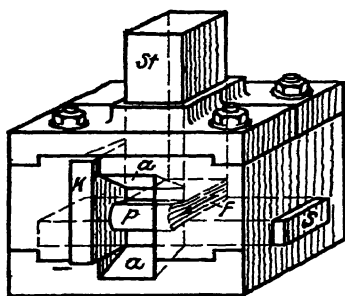FIG. 16.—POLE FIGURE FOR MOST DENSELY PACKED RHOMBIC DODECAHEDRAL PLANE OF COLD-ROLLED IRON.

FIG. 17.—APPLIANCE FOR COMPRESSING TEST SAMPLES.

    a. Milled opening.   *P*. Test piece.
    S. Raised sill of mold.   *St*. Plunger.
    K. Wedge to facilitate changing samples.

conditions. These are recorded in Fig. 15 by hollow and solid circles. Both lattice orientations, or if the twin locations are included, the four lattice positions, which we assume, furnish an excellent and complete description of the pole figure.

A determination of the texture of cold-rolled iron as an example of a body-centered cubic metal gives the pole figure of Fig. 16 for the most densely packed rhombic dodecahedral plane. Assigning a rational lattice orientation which will give this texture is considerably simplified by the observation that the spread is of the type of a pure rotation about the direction of rolling. It turns out that the direction of rolling and the cross direction are indexed 011 and that the normal to the foil is a 001 direction. In Fig. 16 this position is given by small circles.

TEXTURE WITH PLANE PARALLELEPIPEDAL COMPRESSION

The crystallographic interpretation of the texture of rolled materials was completely obscure for a while. Therefore it seemed desirable, for

further development, to supplement the study of tensile and compressive textures by a study of the simplest possible, and least equivocal, case of a deformation process of lower symmetry. To this end the rolling process was idealized in terms of a compressive process in which the flow was restricted to one, and just one, direction perpendicular to the axis of the compressive stresses. Such a deformation is secured by plane parallel-epipedal compression.[21]
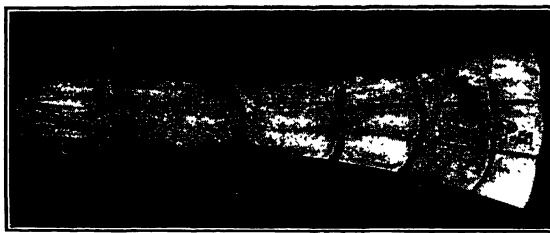

FIG. 18.—ALUMINUM TEST BAR AFTER DE-FORMATION OF 68 PER CENT.

FIG. 19.—IRON TEST BAR AFTER DEFORMATION OF 48 PER CENT.

Aluminum and iron were again selected as materials for the test. The appliance for compressing the test samples is shown in Fig. 17. By means of the milled opening a and the raised sill S of the mold, any increase in the cross-section of the test piece is prevented. S is also used as a stop
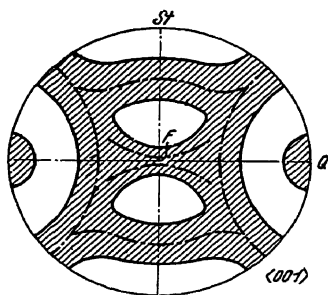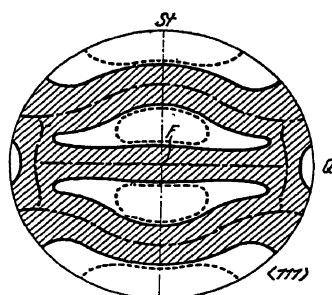

FIG. 20.   FIG. 21.

FIG. 20.—POLE FIGURE FOR CUBE PLANE (001) OF ALUMINUM AFTER 73 PER CENT. DEFORMATION.

FIG. 21.—POLE FIGURE FOR OCTAHEDRAL PLANE (111) OF ALUMINUM AFTER 73 PER CENT. DEFORMATION.

for one of the side walls which is made as a wedge K to facilitate changing the samples. Figs. 18 and 19 show an aluminum and an iron test bar after deformation of 68 and 48 per cent. respectively. A test of the homogeneity of the deformation was made by scribing a rectangular net on the side faces which should remain rectangular and rectilinear.

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[21] F. Wever and W. E. Schmid: *Op. cit.*
Ztsch. f. Metallkunde (1930) **22**, 133.

The texture of samples after severe deformation was completely determined by a large number of exposures at different angles. Figs. 20 and 21 give the pole figures for the cube plane (001) and the octahedral plane (111) of aluminum after 73 per cent. deformation, while Fig. 22 shows the arrangement of the rhombic dodecahedral plane (011) for iron after a deformation of 48 per cent. The intensity maxima, and therefore the distribution maxima, are shown by the long and short dashed lines.

FIG. 22.—ARRANGEMENT OF RHOMBIC DODECAHEDRAL PLANE (011) FOR IRON AFTER 48 PER CENT. DEFORMATION.

ANALYSIS OF THE TEXTURES

Deformation of Single Crystals of Face-centered Cubic Metals

The following observations are based on the slip mechanism of aluminum, which has been studied in particularly great detail but, even so, the same observations can be extended to other cases. The process here follows the laws of deformation by "translation" which were early established by Mügge[22] for crystalline minerals. The slip planes are found to be the four octahedral planes (111), in each of which there are three directions of slip 011 so that in all there are 12 systems of slip. Slip on other planes and in other directions has not been observed in aluminum and appears not to occur in other face-centered cubic metals.[23]

The production of slip on a slip plane requires the application of a fixed minimum shearing stress along one of its three directions of slip. This holds in general for the different metals. This minimum stress is raised by the deformation of the crystal, and indeed, as Taylor has shown for aluminum, by about the same amount on both the active and inactive slip planes; the inactive slip planes are somewhat *more* strengthened than those which actually support slip.

The extension or compression of a single crystal by applied stress produces a definite alteration in the external shape. This does not necessarily conform to the change in shape produced by slip along the slip system bearing the greatest shearing stress. From this behavior moments arise which tend to rotate the active directions of slip into the direction, or directions, of flow of the metal caused by the external change in shape.

There arise two possible ways in which the crystal can accommodate itself to the forced change in shape. Either the applied stresses are
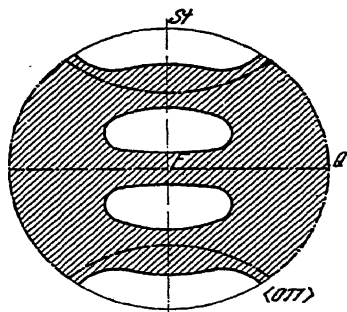
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[22] O. Mügge: *Neues Jahrbuch f. Min., Geol. und Palaeontologie* (1895) **2**, 211.

[23] C. F. Elam: *Proc.* Roy. Soc. London (1926) **A112**, 289.

Proc. 2nd. Int. Cong. for Applied Mechanics, 258. Zurich, Sept. 1926.

sufficient to produce slip on other slips which have not hitherto functioned, or else they produce rotations in the crystal. Of these two cases, the latter generally happens. The manner and extent of the lattice rotation can be easily calculated from the externally forced change in shape.[24] If the deformation does not proceed uniformly throughout the entire crystal, the difference in the rotation of the individual portions is caused by a bending movement, or a translation along elastically bent lamellae. This process, the so-called "bending slip" or *Biegegleitung*, has been established as the basis of the deformation of metallic single crystals by Mark, Polanyi and Schmid.[25] If Taylor and coworkers did not observe such bending movements in their investigations, it is to be explained as due to such careful manipulation of the crystal that a perfectly homogeneous deformation was obtained in the region observed.

The rotation of the crystal, with respect to the applied forces, changed the shear stress in the individual slip planes and in the directions of slip. As the deformation progresses, slip may occur on a second or even on a third system in addition to the original one, each time associated with a rotation of the lattice. Such a "competition" of slip planes was first observed by Taylor and Elam[26] and, as careful investigation has shown, can be explained as coincidental slip on the individual slip planes with corresponding lattice rotations.

Deformation of a Crystallite inside a Polycrystalline Aggregate

The plastic deformation of a polycrystalline aggregate proceeds by the functioning of the fine mechanism of deformation of the crystallites excluding the inconsequential displacement at the grain boundaries. The deformation of the individual grain is not rigidly forced from without but follows from its accidental location and shape and from the concurrence of the different slip movements and "bendings" in all the neighboring grains, and it is the superposition of these individual deformations in certain larger regions that forces the external deformation. The formation of a uniform texture which contains the symmetry relationships of the macroscopic deformation process justifies us in assuming a uniform stressing of all the grains on the average. As a basis of the statistical treatment of a large number of grains in a homogeneous structure which is uniformly strained, we can use the external stress field as a mean value of the fields in the grains. The shearing stresses for the different slip systems of a grain in a polycrystalline aggregate will be the same, on the average, as if the grain were directly subject to the macroscopic field of force.

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[24] R. Weissenberg: *Ztsch. f. Krist.* (1924–1925) **62**, 58.

[25] H. Mark, M. Polyani and E. Schmid: *Ztsch. f. Physik* (1922) **12**, 58.

[26] G. I. Taylor and C. F. Elam: *Proc.* Roy. Soc. London (1923) **A102**, 643. *Ibid.* (1925) **A108**, 28.

On the other hand, there exists a fundamental difference between the two cases in respect to the rotation of the lattice. While with the single crystal this is imposed by the external change in shape, crystallites in an aggregate are given an opportunity to exhibit the individualities of their slip mechanisms in the cross play of all the different movements by slip and bending between neighboring grains. *Contrary to the customary explanation, we ascribe greater freedom to the grains of a polycrystalline aggregate than to the single crystal which is deformed in the usual way by gripping the ends.* In the aggregate, in the course of the concurrent deformations of neighboring grains in a certain region, the grain bends about an axis about which it has a particularly low resistance to bending.

One definite type of plastic deformation is associated with the mechanism of translation, as was first shown by Mügge[27] and later by Gross[28] and Leonhardt. Here the crystals break up by slip into elastically bent lamellae. The slip planes are bent cylindrically about an axis perpendicular to the active direction of slip; therefore the preferred axis of this bending movement lies in the plane of slip perpendicular to the direction of slip.

The following propositions hold for the mean behavior of any crystallite in a polycrystalline aggregate which is subjected to a macroscopically homogeneous deformation:

1. Those slip planes and directions of slip are selected for which the shearing stress is a maximum with respect to the external forces impressed.

2. The crystallite will rotate about an axis which is in the plane of slip and perpendicular to the direction of slip, and in a direction that will lessen the angle between the direction of flow of a particle and that of the next adjacent particle.

THE DEFORMATION TEXTURE

Slipping and rotation of the crystallites produce the deformation texture. By assuming uniform strengthening within the individual crystallites, the laws developed above can be applied to the whole process of deformation. The texture is formed from those "stable" positions of the crystallites for which no further rotation occurs, according to the propositions 1 and 2. In contrast to the "ideal" positions customarily assumed in describing this effect, we should assume that there are whole series of stable positions particularly for deformation processes of low symmetry. These are found with the use of these principles by systematically following the average deformation processes for all the crystallite positions of a polycrystalline aggregate.

Certain simple principles can be predicted for them. It is always characteristic of a stable position that either all of the slip systems are

[27] O. Mügge: *Ztsch. f. Krist.* (1924–25) **62**, 100.
[28] R. Gross: *Ztsch. f. Metallkunde* (1924) **16**, 18.

free of shearing stress, a possibility that exists only exceptionally as with metals with only one slip plane, or else a "competition" exists between the several systems which nullify the rotation effects. In this case the following conditions hold:

1. The shearing stresses must be equal for at least two systems of slip, and larger for these than for any other.

2. The lattice rotation corresponding to slip along the most highly stressed system must alter the shearing stresses to produce slip along one of the other systems.

3. The rotations which arise in the course of the competition must cancel each other.

The first condition shows the importance that attaches to the orientations for which the symmetry elements of the deformation process coincide with those of the crystallites and produce several slip systems with maximum shearing stress which are symmetrically situated in the field of force. If the corresponding lattice rotations cancel out, condition 3 is satisfied and it only remains to see whether the orientation is stable or labile by means of the second condition. The ideal positions that characterize axially symmetrical processes are in part particularly simple stable ones. In the following, a complete development will be given of all possible stable positions of these types of deformation, and in that way it will be proved that a complete description of the texture is given by these ideal positions.

Development of Axially Symmetrical Textures of Face-centered Cubic Structures

In an axially symmetrical deformation process, the position of a crystallite is definitely given by the location of the lattice with respect to the axis of the deformation. If this axis be allowed to assume various directions at random with respect to a stationary crystallite, each of these orientations corresponds to a fixed crystallite position within the aggregate. In the same way in the pole figure of a single crystal a fixed position of the deformation axis, with respect to the lattice, can be correlated to each point of the polar sphere and thus obtain a simple representation of all possible crystallite positions. With a cubical lattice with its simple type of symmetry, it suffices to reproduce the section of a circular triangle of a cube plane and two rhombic dodecahedral planes (*ABC* in Fig. 23).

A calculation of the shearing stresses in the different slip systems of a crystallite gives the slip plane and the direction of slip that are most highly stressed for each orientation with respect to the deformation axis. By means of the method of representation described above, we can assign the active slip system and the corresponding crystallite orientation to each point of the polar sphere and, in this way, divide the sphere into regions

in which slip is of the same type. Taylor and Elam have done this for the face-centered cubic lattice (Fig. 6). At the same time all of the crystallite orientations that correspond to the points of one of the spherical triangles just mentioned are characterized by the same direction of slip on the same plane, while the lattice rotation is about the same axis and in the sense that the angle between the active direction of slip and the direction of flow of the next adjacent material decreases. In Fig. 24, this change in orientation of the crystallites for the triangle *ABC*, with respect to its surroundings, is given by the single arrows for a tensile process and by the double arrows for a compressive process. It is easy to see that this rotation of the lattice places the deformation axis first
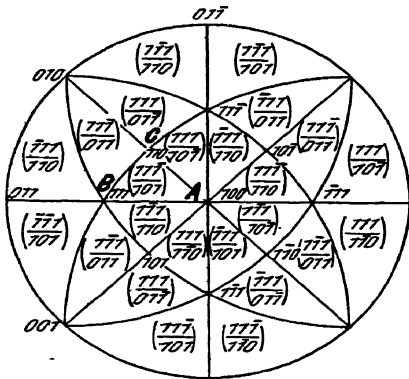

FIG. 23. FIG. 24.

FIG. 23.—CRYSTALLITE ORIENTATION OF ALUMINUM (AFTER TAYLOR AND ELAM).
FIG. 24.—CHANGE IN ORIENTATION OF CRYSTALLITES FOR TRIANGLE ABC OF FIG. 23 UNDER STRESS.
Single arrows indicate change for a tensile process; double arrows for a compressive process.
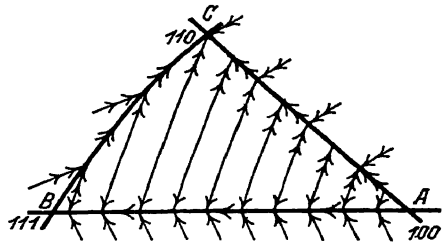
in a plane of symmetry between two active slip systems, while it may also be seen how it is that in the course of this competition these two slip actions result in a final position of stability. This gives a 111 direction for the deformation axis in tension and a 011 direction for compression, which agrees with experiment.

Texture of Plane Parallelepipedal Deformation

If we now attempt to synthesize the texture of plane parallelepipedal deformation, it becomes apparent that the viewpoint developed here and the information obtained do not suffice. With axial symmetrical processes simple seriations of the orientations of the crystallites could be recognized for which two slip systems of equal and maximal shearing stress were characteristic, and through which a crystallite would have to pass during the competition between two directions of slip (Fig). 24.

The rotation of the lattice which comes from the concurrence of shifting slips is fixed by the condition of equal shear on the competing slip systems. On the other hand, it follows from the twofold, infinite multiplicity of positions assumed by the crystallites in a stress field of several axes that a fixed crystallite position with two equally stressed slip systems will be surrounded by an infinite number of others for which this condition is likewise satisfied.   The resulting rotation of a crystallite can be judged only with the knowledge of the strengthening process that controls the shifting from one of the competing systems to the other.

But the external stress field is also not understood.   In addition to the applied compressive force, which is known, we have the pressure on the side walls.   Its magnitude is determined by the condition that no lateral
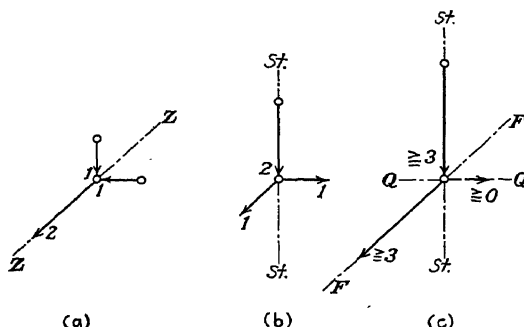

FIG. 25.—THREE-DIMENSIONAL STRESSES.
a. Axial symmetrical tension.
b. Axial compression.
c. Plane deformation.

spreading of the test sample occurs, and therefore depends on the condition of the test sample.   This, in turn, will vary during the process as a result of the formation of the texture, not only absolutely but also relatively, to the compressive force.

If, in spite of this, we wish to secure a correlation with the texture of axially symmetrical deformations and, therewith, with the laws governing single-crystal deformation, we can compare the different deformation processes which may be represented by their deviators.   We secure this by reproducing a uniform three-dimensional stress from the tensors of the external stress field equivalent to the mean value of the three major stresses.[29]   For axial symmetrical tension, this gives a tensile stress of two units in the elongation axis Z (Fig. 25), with two compressive stresses perpendicular thereto of one unit each.   For axial compression, it gives a pressure of two units in the compression axis St, with tensile stresses perpendicular thereto of one unit each.   The plane deformation is

[29] A. Nadai: Der bildsame Zustand der Werkstoffe, 168.   Berlin, 1927.   Springer.

represented by a compressive stress $\geqq$ 3 units in the direction of compression and a tensile stress $\geqq$ 3 units in the direction of flow and a tensile stress $\geqq$ 0 in the cross direction. The equality signs hold for the start of deformation of a polycrystalline aggregate, while the formation of the texture shifts the conditions in the direction of the inequalities.

We see that plane deformation can be regarded as a superposition of an axial pressure in the direction of this compression with an axial tension
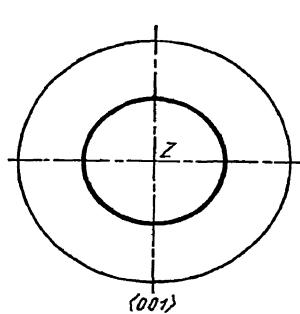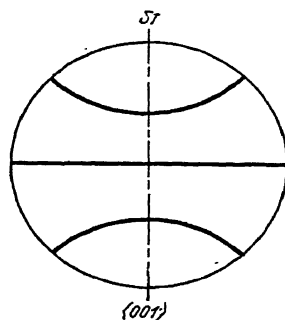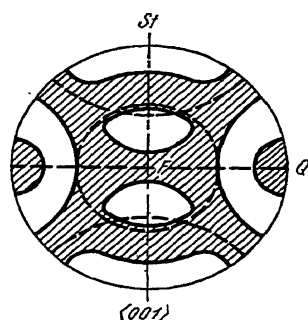

FIG. 26. FIG. 27. FIG. 28.

FIG. 26.—IDEAL POLE FIGURE FOR CUBE OF ALUMINUM.
FIG. 27.—IDEAL POLE FIGURE FOR OCTAHEDRON OF ALUMINUM.
FIG. 28.—APPROXIMATION OF TEXTURE OF PLANE DEFORMATION OBTAINED BY SUPERPOSING FIG. 26 ON FIG. 27.

in the direction of flow. At the start, both components are equally large, but as the anisotropic condition develops in the deformed material, the tensile process diminishes with respect to the compressive process, so that we approach closer and closer to a pure compression. This viewpoint agrees well with an observation of Tammann[30] according to which the deformation in the first stage of rolling corresponds to an axial tension in the direction of rolling, while with greater degrees of deformation, as with axial compression, it goes according to the normal to the direction of rolling.

[30] G. Tammann and A. Heinzel: *Archiv. f. d. Eisenhüttenwes.* (1927–28) **1**, 663.

It is also pertinent to attempt to analyze the texture of plane parallel-epipedal compression in terms of the two axial textures. For this purpose the two ideal pole figures for the cube and octahedron of aluminum are given in Figs. 26 and 27 for the conditions following axial symmetrical compression and stretching. Fig. 28 shows that a good approximation of the texture of plane deformation is obtained by superposing one upon the other. These crystallite positions in the plane-deformed test samples can be classified, for the greater part, as a tensile texture with the directions of flow as the axis and an axial symmetrical texture according to the direction of compression of the plane deformation process.

By a more detailed analysis of the texture with plane parallelepipedal deformation, an attempt was made to explain the observed spread of the positions of the crystallites. This came by utilizing an observation of Taylor and Elam[31] that the active slip systems strengthen somewhat less than the inactive, which means that the shear stress on a second system must become a little larger than on the original system until a competition between the two can be set up.

BODY-CENTERED CUBIC METALS

The application of these principles to a polycrystalline aggregate of body-centered cubic metals is complicated by the circumstance that the mechanism of the deformation is not clearly understood in this case. Osmond and Cartaud,[32] and similarly Tammann and Müller,[33] assume slip on octahedral planes (111) and the same combined with "simple shift" (*einfache Schiebung*) along the icositetrahedral plane (112), while O'Neill,[34] with the same metal, and Goucher[35] and Schmidt[36] with tungsten gave the rhombic dodecahedral plane (011) as the slip plane. Taylor and Elam[37] concluded from an extended study of iron that it possesses a special slip mechanism in which only the direction of slip 111 is determined crystallographically.

According to the structure of the lattice and observations on other lattice types, it is most probable that slip occurs on the most densely spaced plane (011) and in the direction of closest spacing 111.[38] Furthermore, this assumption, taken in connection with the formation of the texture, leads to a conclusion that agrees with experiment. Accordingly in Fig. 23, we are to regard all slip plane normals of the face-centered lattice 011 as directions of slip of the body-centered lattice and, con-

[31] G. I. Taylor and C. F. Elam: *Op. cit.*

[32] F. Osmond and G. Cartaud: *Metallurgie* (1906) **3**, 522.

[33] G. Tammann and A. Müller: *Ztsch. f. Metallkunde* (1926) **18**, 69.

[34] H. O'Neill: *Jnl.* Iron and Steel Inst. (1924) **109**, 93.

[35] F. S. Goucher: *Phil. Mag.* (1924) **48**, 229.

[36] Schmidt: Aetz-und Loesungserscheinungen an Wolfram Diss. 1924. Greifswald.

[37] G. I. Taylor and C. F. Elam: *Proc.* Roy. Soc. London (1926) **A112**, 337.

[38] M. Polanyi: *Ztsch. f. Physik* (1923) **17**, 42.

versely, all directions of slip 011 as slip plane normals. The shearing stress on a slip system determined by two of these directions is equally large for both cases, so that we get the same subdivision of the polar sphere in the region of uniform slip, as with the face-centered lattice. Furthermore, the bending axis is the same both times and it is only the direction of the lattice rotation that reverses by interchanging the slip plane normal and the direction of slip. Accordingly Fig. 24 represents the change in orientation of the crystallites in a body-centered cubic structure if we represent the axial compression by the single arrow and the tensile process by the double arrow. In agreement with experiment we find 011 in the tensile axis as the result of the rotation, and 111 in the
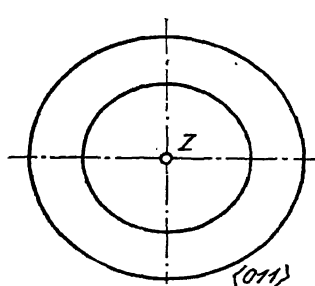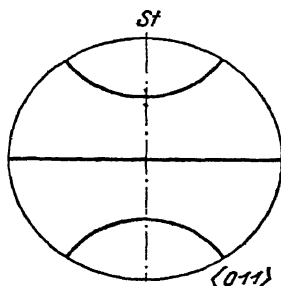

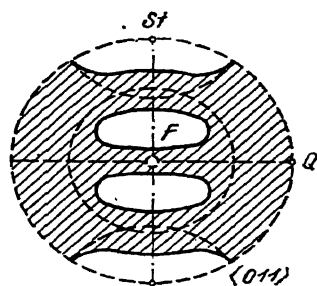FIG. 29.   FIG. 30.   FIG. 31.

FIGS. 29 AND 30.—IDEAL POLE FIGURES OF TWO DEFORMATION TEXTURES WITH AXIAL SYMMETRY FOR RHOMBIC DODECAHEDRON (011).

FIG. 31.—IDEAL POLE FIGURE OF TEXTURE WITH PLANE PARALLEL DEFORMATION.

direction of compression of the compression process. This accounts very clearly for the outstanding fact that the axial tension and compression texture reverse for face-centered and body-centered structures.

The ideal pole figures of the two deformation textures with axial symmetry are reproduced in Figs. 29 and 30 for the rhombic dodecahedron (011). It is also evident here that the texture with plane parallel deformation (Fig. 31) can be constructed from parts of the two axially symmetrical textures. Since it was not possible, on account of experimental reasons, to investigate more than one kind of plane of comparatively great multiplicity, there is some uncertainity as to the precise limits of the region containing the axially symmetrical texture. For the same reason the spread of the results could not be considered. The crystallite orientations of an axial compression texture with respect to the direction of compression in the plane deformation are, without exception, compatible with the pole figure obtained while of those of a tensile texture taken with respect to the direction of flow it is only the orientation of which the 011 direction is not more than about 60° to the cross-section that is in agreement with experiment.

CORRELATION WITH THE ROLLING PROCESS

As has been stated, the plane parallel deformation can be regarded as an idealization of the rolling process. The close relationship of the two kinds of deformation is expressed in their textures, as is shown clearly by comparing their pole figures (Figs. 32 and 33). From this we may reasonably assume that the texture of the rolling process has similar close relationships to textures with axial symmetry that were found with plane parallelepipedal deformation. They are less conspicuous, however, on account of the complex and heterogeneous flow of material, so that a detailed analysis is not possible.
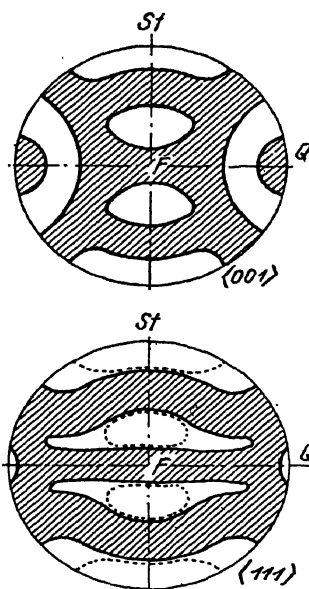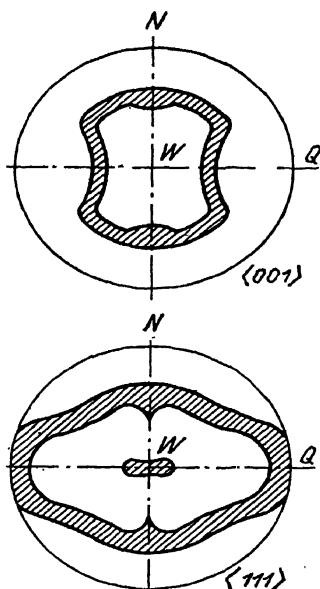

FIG. 32.   FIG. 33.

FIG. 32.—POLE FIGURE OF TEXTURE PLANE PARALLEL DEFORMATION.
FIG. 33.—POLE FIGURE OF TEXTURE OF DEFORMATION BY COLD ROLLING.

SUMMARY

1. Starting with the conception that only a complete and unprejudiced interpretation of the X-ray data can appropriately serve as the basis for the deduction of the relationships between the orientation of the crystallites in a cold-worked metal and the inner slip mechanism of that metal, a new method for describing conditions of statistical anisotropy with the aid of pole figures was described. The simple relationships of these figures to the X-ray diffraction patterns are shown and an example is discussed which shows the conversion of the X-ray patterns to pole figures by means of graphic charts.

2. The formation of the texture by drawing, cylindrical compression, rolling and plane parallel compression was described by means of pole figures for the limited case of cubic metals with face-centered and body-centered lattices.

3. The known laws of plastic deformation of face-centered cubic single crystals are used to elucidate the deformation process of a crystallite in a structure. In this, particular importance was given to the mechanism of the plastic bending of the crystal. Systematically following the changes in position of randomly orientated crystallites in an axially symmetrical deformation process leads to a texture which is found experimentally to contain those crystallite orientations, in stable or labile positions, for which no further lattice rotation occurs.

4. The texture of aluminum after plane parallel deformation is described as a superposition of parts of textures produced by axially symmetrical tension and compression with their axes respectively in the direction of flow and of compression of the deformation process.

5. Crystallite positions which were found by experiment to differ from those which are to be expected from theoretical considerations were investigated by means of various deformation textures of aluminum and the findings were accounted for by means of the processes of deformation and strengthening of single crystals.

6. Propositions 3 and 4 are extended to the body-centered cubic structure under the assumptions that the (011) plane is the plane of slip and that the direction 111 is the direction of slip.

7. Inasmuch as plane parallel deformation is closely related to the rolling process, which is also confirmed by the similarity of their textures, we arrive at a unified viewpoint from which to consider the important deformation textures. Its basis lies in the well-known mechanism of deformation of single crystals.

DISCUSSION

(Sam Tour presiding)

C. S. BARRETT, Washington, D. C.—One of the reasons for the excellence of this paper is the critical attitude Dr. Wever has taken toward the work he is reviewing, and his endeavor to draw only rigorous conclusions from experimental data. His method of presenting deformation structure data makes it possible to see clearly just what the experimental data are and how closely theory is in accord with them.

The author mentions that a number of photographs and considerable drafting work are necessary in determining a pole figure. To lessen this work he has prepared charts (Figs. 4, 5 and 6) for certain sets of conditions. When changing substances, wave lengths or atom planes, however, new charts must be prepared for each new set of conditions.

A direct method of plotting pole figures not requiring the preparation of these charts should perhaps be mentioned. A stereographic projection may be used with the X-ray beam entering the projection sphere at point A of Fig. 34. A reflection

circle C, of suitable radius for planes of the form $\{hkl\}$ is drawn, with its center at A. The diffraction pattern is placed centrally over this chart and radial lines passing through $\{hkl\}$ spots of the pattern are made to intersect the reflection circle. The intersection of these radii and the reflection circle form the stereographic plot of the reflecting planes. (In Fig. 34, film-spot B is caused by a plane whose orientation is represented stereographically by point B'.) This plot is referred to the direction of the X-ray beam, not the orientation of the specimen, as is desired. However, if one rotates the plot for each pattern, by means of a stereographic rotation net, an amount corresponding to the rotation of the specimen from its standard position when that pattern was made, the final desired pole figure is obtained. With this method the only thing that needs to be altered when one alters substances, wave length or planes is the radius of reflection circles which is, of course, simple to do.
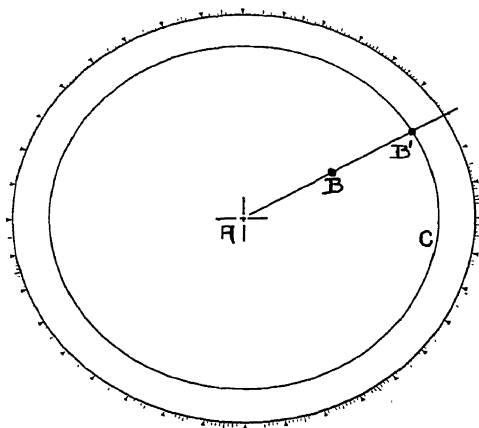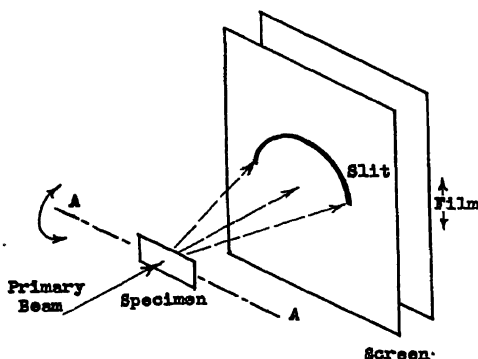

FIG. 34.   FIG. 35.

There is an alternative method of obtaining pole figures that has occurred to me, involving a simple mechanical device. In Fig. 35, a beam of X-rays is made to strike a specimen mounted so as to oscillate about an axis AA. A photographic film is supported so as to shift up and down, and is mechanically coupled to the specimen so that it will shift up and down in phase with the oscillations of the specimen. A shield with a semicircular slit is placed between the specimen and the film, to allow only certain of the diffracted rays to reach the film. The pattern on the film, which would be read by means of charts placed over the film, would give directly the desired pole figure.

It should be possible with this apparatus accurately to determine a pole figure with only a few pictures and with a minimum of drafting work. Another advantage to be expected from such a device is that it would bring out the fine structure of pole figures, when any exists, because the continuous oscillation of the specimen would cause the reflection circle to sweep continuously over regions of the polar surface instead of crossing it at a finite number of places. I am planning to try this method soon in connection with Widmanstätten structure problems, where it is necessary to detect this sort of fine structure.

L. W. McKEEHAN, New Haven, Conn.—In discussing a long paper like this, it is perhaps of advantage to mention the two or three things that are strikingly new and worth thinking about, and the most important of these probably is the author's

emphasis on the freedom of a small crystallite in the midst of a test piece undergoing deformation.

In earlier studies it was customary to think that every crystal was subject to the same conditions. That, of course, is very far from being the case. Dr. Wever points out that the distribution of stress as a function of crystallite position and crystallite orientation is one of the controlling circumstances that set up the momentary position of that crystallite. The final result is not a parallel arrangement of all of them. The distribution is just as much a part of the result as the most probable position, and the study of single crystals will not tell all that will happen in an aggregate of crystals.

Another important point is that the special type of deformation that may be applied is only in rare cases simple enough to be analyzed completely. In the single case of tension it was possible here.

In regard to the comment of Dr. Barrett on the diagrams, I do not think Dr. Wever's diagram is much more complicated than Dr. Barrett's Fig. 34. In the middle of Fig. 4, there is a circle with several dots on it. That is the circle, inside the stereographic base circle, which Dr. Barrett has drawn. The other heavy-line circles of different diameters, displaced right and left from the central circle are the positions obtained by his construction in which the whole circle is rotated right or left about the vertical axis, so that what Dr. Wever has done is to carry out the construction for a complete circle several times, six or seven times in these figures, and then to avoid making the construction again.

W. P. Davey and C. B. Hollabaugh, State College, Pa. (written discussion).—This paper is an excellent presentation of the present status of this work and is worth the careful study of all experimenters in the crystal structure of metals. Wever has been a pioneer in crystal structure work and has probably made more, and better founded, contributions to the study of plastic deformation in metals than any other one man. We are especially pleased to see his work on pole figures given such prominence in this country.

Our experimental work in the School of Chemistry and Physics of The Pennsylvania State College seems to have shown that the face-centered cubic metals do not all behave alike when rolled, and that aluminum is much more sensitive to slight differences in rolling technique than the other common metals of this group. Our work has shown that copper and nickel are relatively insensitive to slight differences in technique. It seems to us, therefore, that the choice of one of these two metals would have been more fortunate than that of aluminum for Dr. Wever's investigations, especially if generalizations are to be made from the data.

F. Wever (written discussion).—I wish to thank Dr. Barrett for his statement that the pole figures of deformation structures could be photographed directly, using simple arrangements. As early as 1930, O. Kratky[39] described a series of methods for this purpose, among which may be found the one proposed by Mr. Barrett. I agree with Professor McKeehan that these methods do not imply a great simplification in the study of structure, and therefore they are hardly worth the trouble they cause. I agree with Messrs. Davey and Hollabaugh that one of the most important difficulties encountered at present in a satisfactory interpretation of structure on a purely crystallographic basis is that isomorphic metals under the influence of unknown secondary circumstances may differ greatly from each other in their action during deformation.

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[39] O. Kratky: *Ztsch. f. Krist.* (1930) **72**, 529.

Studies upon the Widmanstätten Structure, I.—Introduction. The Aluminum-silver System and the Copper-silicon System*

By Robert F. Mehl† and Charles S. Barrett,‡ Washington, D. C.

The importance of the Widmanstätten structure to structure theory in metallography has been recognized by many writers.[1]

It is a structure produced by the precipitation of a new phase from a solid solution upon cooling as a result of changing solid solubility, and displays a characteristic appearance indicating a crystallographic relationship between the new phase and the original solid solution (Fig. 1). First discovered in 1808 by Alois de Widmanstätten[2], the structure has been traced by analogy through many alloy systems. Particularly is this true of the steels. Sorby's classic work[3] on the microstructure of iron and steel was in essence an attempt to explain the origin of this characteristic structure in meteoric iron. He observed in a Bessemer steel and in a cast-steel ingot structures which we now recognize as typical Widmanstätten figures.[4]

Osmond[5] observed structures in a steel ingot analogous to those found in meteorites. Arnold and McWilliam[6] obtained (and recognized) a

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† Superintendent, Division of Physical Metallurgy, Naval Research Laboratory.

‡ Assistant Physicist, Division of Physical Metallurgy, Naval Research Laboratory.

[1] See, for example, the chapter on cast steel in Professor Sauveur's Metallography and Heat Treatment of Iron and Steel, 156–166. New York, 1926. McGraw-Hill Book Co.

[2] Director of the Imperial Porcelain Works in Vienna. Widmanstätten polished and etched a surface upon a meteorite known as the Agram Iron and observed the structure since known in his honor as the Widmanstätten figure or structure. Widmanstätten attempted, apparently, no explanation of this structure, and in fact did not publish an account of his discovery, though it shortly became known among crystallographers and mineralogists.

[3] H. C. Sorby: On the Microscopic Structure of Iron and Steel. *Jnl.* Iron and Steel Inst. (1887) **30**, 255–288. Sorby's work extended over a period of 20 years preceding this date.

[4] H. C. Sorby: *Loc. cit.*, Figs. 12 and 13.

[5] F. Osmond: Sur la Cristallographie du Fer, 24. Paris, 1900.

[6] J. O. Arnold and A. McWilliam: Thermal Transformations of Carbon Steels. *Jnl.* Iron and Steel Inst. (1905) **68**, 35.

well-defined Widmanstätten figure in a cast hypoeutectoid steel containing 0.39 per cent. carbon.

FIG. 1.—SECTION OF CASAS GRANDES METEORITE.   × 1.
Analysis: Fe, 95.13 per cent.; Ni, 4.38; Co, 0.27; P, 0.24.   Polished.   Etched with nitric acid.   Original in National Museum, Washington, D. C.

N. T. Belaiew,[7] in 1908, synthesized a remarkably well-formed Widmanstätten figure in a 0.55 per cent. C steel. Many unsuccessful attempts had been made deliberately to synthesize the Widmanstätten

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[7] N. T. Belaiew: *Verhalt. Russ. Min. Gesell* [2] (1909) **47**, 209–231.

N. T. Belaiew [On the Genesis of the Widmanstätten Structure in Meteorites and in Fe-Ni and Fe-C Alloys. *Mineral Mag.* (1923–1925) **20**, 173.] discusses at length the factors contributing to the formation of well-defined Widmanstätten figures. Belaiew limits the term Widmanstätten figure to the intragranular structure, and uses the term Widmanstätten structure to describe the appearance of the multigranular structure in which each grain exhibits the Widmanstätten figure. This convention in nomenclature will be adopted throughout this and succeeding papers, though for reasons that will appear later the Widmanstätten figure sometimes will be designated as a precipitation structure. Excellent photographs of Widmanstätten figures in Fe-C alloys have been published by Hanemann and Schrader in *Atlas Metallographicus*. Gebrüder Borntraeger, Berlin, 1929.

figure in Fe-Ni alloys.[8] In 1909, however, C. Benedicks[9] successfully reproduced the Widmanstätten figure (albeit upon a much smaller scale) in an artificial Fe-Ni alloy containing 11.7 per cent. nickel.

Structures analogous to those in steel and in meteorites have often been noted in other alloy systems. For many years they have been observed in Muntz metal (60 per cent. Cu, 40 per cent. Zn), designated ordinarily as "cleavage structures."[10] In a discussion of a paper by Belaiew, Portevin[11] lists many alloys showing this structure, culled from among the photomicrographs of alloys published in the *Zeitschrift für anorganische Chemie*.

It must not be assumed that the Widmanstätten figure is peculiar to metallic alloy systems alone. It has been observed frequently in purely nonmetallic systems. In great perfection it may be found in alloys of hematite and magnetite.[12] It has also been noted[13] in alloys of FeS and MnS, and it is not to be doubted that such structures can be produced in any system of crystalline phases that fulfills the conditions outlined below,[14] nor can it be doubted that the formation of this structure illustrates the operation of some underlying and fundamental crystallographic mechanism common to all solid-solid transitions.

These structures have been variously designated. Most frequently they are called "acicular," or "needlelike" (usually unfortunate terms,

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[8] Meteorites exhibiting the Widmanstätten figure are Fe-Ni alloys containing in the neighborhood of 8 per cent. Ni. Frequently they are "unigran"; that is, the kamacite lamellae show no change in direction along any surface in the meteorite, and there is no sign of grain boundary in the usual sense. It is, however, not uncommon to find meteorites of this composition built up of many grains. The Widmanstätten figure in meteorites has been comprehensively discussed by L. Fletcher [An Introduction to the Study of Meteorites, British Museum, 1908]; N. T. Belaiew [*Mineral Mag.* (1923–1925) **20**, 173]; L. H. Borgstrom [On the Composition of the Meteoric Nickel Iron Alloys and on Magnetic Lines on Sections of Meteoric Irons. *Fennia* (1925) **45**, No. 2.] The recent study by R. Vogel [Über die Struktur der Eisen-Nickelmeteoriten. *Ztsch. anorg. Chem.* (1925) **142**, 193.] of the metallography of natural and artificial Fe-Ni alloys is very comprehensive.

[9] C. Benedicks: Eine Synthese von Meteoreisen. *Intl. Kong. f. Bergbau, Hüttenweise*, etc. Düsseldorf (June, 1910).

Synthese du fer Météorique. *Nova Acta* Regiae Societatis Scientiarum Upsalinesis [4] (1910) **2**, No. 10, 1–26.

[10] Among recent papers, for example, L. R. van Wert: Some Observations in Heat Treatment of Muntz Metal. A. I. M. E. *Tech. Pub.* 180 (1929).

[11] A. M. Portevin: Discussion. *Jnl.* Inst. Metals (1914) **12**, 52.

[12] G. M. Schwartz: Iron-ore Sinter. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 39. This was known as early as 1863 (G. Rose).

[13] Z. Shibata: Equilibrium Diagram of the Iron Sulphide-Manganese Sulphide System. *Tech. Repts.* Tohoku Imp. Univ. (1928) **7**, 279.

[14] No attempt will be made in this paper to list all of the examples of the Widmanstätten figure that may be discovered in the literature. Although interesting, such a bibliography would be very extensive.

as we shall see), "cleavage structures," and perhaps less frequently "Widmanstätten figures (or structures)."

GENESIS OF THE WIDMANSTÄTTEN FIGURE

The genesis of the Widmanstätten figure is now well understood.[15] Osmond and Cartaud's clear statement[16] years ago still commands respectful attention: "When a body, liquid or solid, deposits successively several solid phases, the secondary or tertiary deposits lodge preferentially between certain crystallographic planes determined by the primary crystallization and thus illustrate its structure."

FIG. 2.—PHASE RELATIONS FOR FORMATION OF THE WIDMANSTÄTTEN FIGURE

The requirements of constitution laid upon alloy systems for the formation of this structure are represented upon an idealized diagram in Fig. 2. Every alloy which shows a Widmanstätten figure has undergone a transition similar to that indicated by the arrow. Thus, in hypoeutectoid steel the high-temperature form is austenite with the γ iron lattice (α in Fig. 2) and the precipitated phase is ferrite with the α iron lattice (β in Fig. 2); in hypereutectoid steel the high-temperature form is again austenite with the γ iron lattice and the precipitate cementite, Fe_3C; in Muntz metal the high-temperature form is β brass, the precipitate α brass.

Despite the fact that it is somewhat anticipating results not reported in this paper, it seems advisable to restate the proposition of Osmond
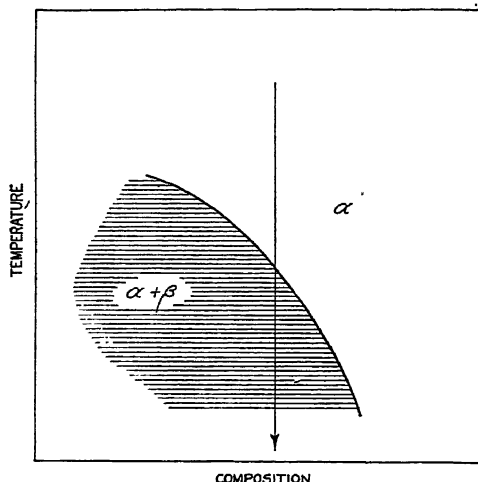
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[15] Although the figure was a subject of much discussion during the nineteenth century the true origin of the structure was not understood, mineralogists and crystallographers apparently thinking that kamacite, taenite and plessite deposited in some sequence of precipitation from a melt, though in no case is there any explicit statement. The true explanation was first given by Osmond and Cartaud in 1904 [Sur les fers météoriques. *Rev. de Mét.* (1904) **69**; also *Compt. rend.* (1903) **137**, 1057.] who, having consulted Roozeboom, published the first concentration-temperature diagram of the Fe-Ni system. The formation of the Widmanstätten figure in meteorites was then correctly ascribed to a precipitation of kamacite (α-Fe solid solution) in plates along certain (octahedral) planes in the original high-temperature solid solution. True knowledge of the formation of the Widmanstätten figure thus dates from the work of Osmond and Cartaud in 1904.

[16] F. Osmond and G. Cartaud: Sur la cristallization du fer. *Rev. de Mét.* (1906) **3**, 491.

and Cartaud in more general terms: When a solid solution, stable at high temperatures, upon cooling precipitates a new phase, this new phase appears in a particular manner; it deposits in such a way that its lattice bears a definite crystallographic relation to the lattice of the parent solid solution.[17]

It should be pointed out that the figure could be produced on heating—as, for instance, when the direction of the arrow in Fig. 2 indicates an increase in temperature—though little attention has been given to this possibility. The effect of increasing temperature would naturally be partly or completely to spheroidize the precipitate, rendering this type of process rather unsuitable for study.

The Widmanstätten figures that have been accurately described in the literature—in the steels and in meteorites—have a plate structure which appears on the surface of polish as a network (Fig. 1). Since it has been shown in these cases that the precipitated plate is parallel to certain crystallographic planes in the parent solid solution, and since any crystallographic plane with Miller indices (hkl), such as for instance the octahedral face, has several other entirely equivalent but nonparallel planes (other octahedral faces in this instance), any one type of crystallographic plane will appear on the surface of polish as a series of intersecting directions, producing the characteristic network display shown in Fig. 1.

The conditions outlined above are the only ones laid upon the constitution of the alloy; an alloy which meets these conditions will permit the development of a Widmanstätten figure. It is necessary, however, that a suitable heat treatment be given the alloy in order to develop the structure to a high degree of perfection, since it is known, for example, that a long time anneal or a very slow rate of cooling after the transformation curve has been traversed may result in an agglomeration or partial spheroidization of the deposited plates, presumably because of surface tension effects and the requirements of minimum surface energy. On the other hand, too rapid cooling will often prevent the segregation of any considerable amount of material and a fine-grained structure (martensitic), often of indistinct appearance, may result. These conditions have been discussed by Belaiew.[18]

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[17] It will be noted that this statement does not postulate the formation of plates. Although the figure actually consists of plates in the steels, in meteorites, and in most other alloys (in which the figure has usually been mistakenly described as needlelike or acicular), proof will be furnished in following papers that in certain cases the new phase may appear in forms other than plates.

The above statement of the formation of the Widmanstätten figure has therefore been given a more general form, expressing the basic fact in the formation of all Widmanstätten figures. It represents, then, a revision of Osmond and Cartaud's statement.

[18] N T. Belaiew: *Mineral Mag.* (1923–25) **20,** 173.

As metallographers are well aware, the appearance of a new phase resulting from a solid-solid transition ("secondary crystallization") may either come within the grain, producing a Widmanstätten figure, or at the grain boundary. Ordinarily both processes are operative. The segregation at the grain boundary is favored by a slow rate of cooling through the critical temperature which affords time for diffusion. A faster rate of cooling, on the other hand, forces precipitation to take place "on the spot," producing a Widmanstätten figure. Even in this case, however, the rate of cooling must not be too fast, else there will be a quenching effect with development of a poorly defined figure.

Furthermore, "the larger the crystalline grain the more difficult it will be for the precipitate to collect wholly at the boundary and therefore the greater the probability of obtaining a Widmanstätten figure."[19]

To summarize, a controlled rate of cooling, neither extremely fast nor extremely slow, a rate probably characteristic of each alloy, and a large grain size are conditions favorable for the development of a well-defined Widmanstätten figure.

The Widmanstätten figure is, then, most clearly seen in cast or slowly cooled alloys. In such cases the segregation of the precipitated phase is sufficiently complete to make its metallographic identification unmistakable. There are structures in other alloys, however, which possibly could best be grouped together as quasi-Widmanstätten figures. These are alloys quenched from a homogeneous solid solution field and observed either in this form or after heating to moderate temperatures. In this group belongs martensite, for under suitable magnification martensite reveals a structure that suggests that the new phase (or phases), which appears during the decomposition of austenite, forms first along the crystallographic planes of the original gamma phase, austenite.[20]

The martensitic type of structure is not limited to the steels but may be formed by a similar heat treatment in nonferrous alloys,[21] though

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[19] N. T. Belaiew: *Idem.*

[20] See, for example, F. F. Lucas: The Microstructure of Austenite and Martensite. *Trans.* Amer. Soc. Steel Treat. (1924) **6**, 669. The importance of the Widmanstätten figure in theories of the austenite-pearlite transformation and of the hardening of steel has been pointed out in a series of papers by A. Sauveur [The Widmanstätten Structure of Iron Alloys. *Proc.* Amer. Phil. Soc. (1927) **66**, 267; Austenite and Its Decomposition. *Trans.* Amer. Soc. Steel Treat. (1930) **17**, 199]. The Widmanstätten figure obtained by Sauveur [The Gamma-alpha Transformation in Pure Iron. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 350] in drastically quenched electrolytic iron cannot be classed as a true Widmanstätten figure from the present point of view, since it is impossible to distinguish two separate phases. The structure obtained by Sauveur could probably better be classed as a quasi-Widmanstätten figure and be regarded as a figure produced by a structural change similar to that forming the true Widmanstätten figure but not leading to a clear-cut segregation of phases.

[21] W. Campbell: Twenty-five Years of Metallography. *Trans.* A. I. M. E. (1926) **52**, 1155.

little study has been devoted to it in these cases. It is quite probable that the mechanism operating in the formation of the martensitic structure is similar to that in the formation of the usual Widmanstätten structure. Frequently, on long-continued heating after quenching, a well-defined Widmanstätten figure will form, as Portevin has shown[22] for Cu-Zn and Cu-Al, and others for other alloys.

The Widmanstätten figure formed on cooling is occasionally not completely developed; *i. e.*, it cannot definitely be resolved and identified under the microscope as composed of two distinct phases. Possibly it is best at the present time to designate these structures as "quasi-Widmanstätten figures." Such, for example, is the case in alloys of gold and magnesium,[23] iron and manganese,[24] and probably also for the "acicular β" observed[25] in alloys of copper and tin and copper and aluminum.[26]

General Significance of the Widmanstätten Figure

The frequent occurrence of the Widmanstätten figure in slowly cooled or cast alloys, and (usually less clearly) in quenched and reheated alloys, and the suggestion that the regularity of its occurrence illustrates the existence of some crystallographic principle at play in solid-solid transitions, makes this structure a proper study in physical metallurgy. It should be pointed out that the conditions for the formation of this figure, as illustrated in Fig. 2, are exactly those necessary for age-hardening. The study of the mechanism underlying the formation of the Widmanstätten figure is therefore intimately related to the study of the aging process.[27]

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[22] A. M. Portevin and G. Arnou: Sur le revenu des bronzes d'aluminium. *Compt. rend.* (1912) **154,** 511.

[23] G. G. Urasow: Auride des Magnesiums. *Ztsch. anorg. Chem.* (1909) **64,** 375.

[24] C. R. Wohrman: Heterogeneity in Iron-manganese Alloys. A. I. M. E. *Tech. Pub.* 14 (1927).

[25] S. L. Hoyt: On the Copper-rich Kalchoids. *Jnl.* Inst. Metals (1913) **10,** 335.

[26] B. E. Curry: Constitution of Aluminum Bronzes. *Jnl. Phys. Chem.* (1907) **11,** 425; H. Hanemann and P. D. Merica: Über Kupfer-Aluminum-Legierungen mit 85 bis 90 % Kupfer. *Int. Ztsch. Metal.* (1913) **4,** 209.

[27] It has not been appreciated generally that the new phase or phases appearing during the aging process in all likelihood take the form of a Widmanstätten figure. R. S. Archer pointed this out [Hardening of Metals by Dispersed Constituents Precipitated from Solid Solutions. *Trans.* Amer. Soc. Steel Treat. (1925) **10,** 718–47] and recently G. Tammann [Discussion. *Ztsch. Metallkunde* (1930) **22,** 146] suggested that the precipitate should take the form of needles. It is obvious, of course, that in the lack of direct evidence, plates or other geometrical forms must be considered equally likely. W. Guertler [Die "Vergütung" oder "Veredelung" von Legierungen. *Ztsch. Metallkunde* (1930) **22,** 83] suggests that the structure of the precipitate is of importance to the aging process.

It seems unlikely, indeed, that any dispersion theory of the aging process should be successful that does not take into account the external form of the precipitated crystallite.

The construction given in Fig. 2 is ubiquitous in alloy constitutional diagrams, and in fact it might be said that most heat treatments, except those having relief of strain or recrystallization for their objective and except possibly those involving purely eutectoid or allied changes, deal fundamentally with the process of crystallographic transformation illustrated by the Widmanstätten figure.

Mechanism of Formation of the Widmanstätten Structure

The discovery of Widmanstätten attracted considerable attention from mineralogists and crystallographers during the last century. G. Tschermak, in his famous Lehrbuch der Mineralogie, published in Vienna in 1885, designates G. Rose[28] as the one who first demonstrated that the kamacite plates forming the Widmanstätten figure in meteorites (Fig. 1) are arranged with respect to one another as the faces of an octahedron. Since that time the figure in meteorites has been known as octahedral in type.[29]

Later Brezina[30] and especially Himmelbauer[31] used graphical methods, including the stereographic, to obtain a more general and complete solution of the problem. It is not clear, however, that any of these writers had the conception that the kamacite lamellae were formed by precipitation parallel to octahedral planes in a crystal stable at high temperatures. They dealt only with the geometry of the kamacite plates and had nothing to say of the mechanism of formation. The true explanation of the mechanism of formation was first given by Osmond and Cartaud, cited above.

Belaiew[32] counted the number of directions exhibited by the ferrite plates in his 0.55 per cent. C steel showing Widmanstätten figures and demonstrated that the maximum number of such directions was four, a proof that no other plane than the octahedral or (111) plane could account for the structure. In addition, Belaiew showed that the angles between the ferrite lamellae upon the plane of polish could be accounted for by an octahedral arrangement of the lamellae. This is indirect but

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[28] G. Rose: Beschreibung und Eintheilung der Meteoriten auf Grund der Sammlung im mineralogischen Museum zu Berlin. Berlin K. Akad. d. Wiss. Abhandlungen (1863) 23–161.

[29] Rose's proof consisted in a demonstration that the angles formed by the kamacite lamellae with one another upon the plane of polish were such as could be explained by a sectioning of an octahedron.

[30] A. Brezina: Über die Orientirung der Schnittflächen an Eisenmeteoriten. *Denkschriften* der K. Akad. d. Wiss., Vienna (1882) **44**, 121.

[31] A. Himmelbauer: Orientierung von Schnittflächen an Meteoreisen. Tschermak's *Min. u. Petro. Mitteilung* (1909) **28**, 153.

[32] N. T. Belaiew: Crystallization of Metals, 82. (Univ. of London Press, 1922). The Inner Structure of the Crystal Grain as Revealed by Meteorites and Widmanstätten Figures. *Jnl.* Inst. Metals (1923) **29**, 379.

satisfactory proof of the octahedral nature of the precipitated ferrite structure, as we shall see. Osmond and Cartaud's observations on cleavage or precipitation structures in a manganese steel[33] were incomplete and need only be mentioned. Desch[34] accepts the theory of octahedral precipitation from all face-centered lattices (austenite and the high-temperature solid solution (γ) in meteorites are both face-centered cubic in structure) and suggests that precipitation from the body-centered intermediate (β) solid solution in the Cu-Al system is probably upon the (100) plane, though proof for this is as yet lacking.

Osmond and Cartaud[35] proposed that precipitation in the solid state should take place (in the form of plates) upon the plane "of greatest reticular density," which is, of course, the (111) plane for face-centered cubic metals, and their suggestion is satisfied by meteorites and hypo-eutectoid steels.

Young[36] studied meteorites carefully and completely by X-ray methods. His results are sufficiently important to the present investigation to deserve brief description.

Young demonstrated that the body-centered cubic kamacite which forms the pronounced lamellae in meteorites is parallel to the octahedral (111) plane of the face-centered cubic taenite, which may be regarded as the undecomposed residue of the high-temperature phase. In addition he demonstrated that the (110) plane in the body-centered kamacite was parallel to this octahedral (111) plane, and pointed out that these planes are the densest packed in their respective lattices. Studying the problem more closely he found that there was a very close coincidence in position between the individual atoms on the two planes, and concluded that the (111) plane in the face-centered phase became the (110) plane in the body-centered phase by a simple conversion involving only a slight shift or rearrangement in atom position. Since the spacings on the two planes differ by only 2 per cent., and the concentration of atoms by only 4 per cent., it is clear that the conversion involved only a very slight shift.[37] There is, then, a relation in orientation between

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[33] F. Osmond and G. Cartaud. Sur la cristallisation du fer. *Rev. de Mét.* (1906) **3**, 522.

[34] C. Desch: *Jnl.* Inst. Met. (1929) **39**, 423.

[35] F. Osmond and G. Cartaud. *Idem.*

[36] J. Young: Crystal Structure of Meteoric Iron as Determined by X-rays. *Proc. Roy. Soc.* (1926) **112**, 630.

[37] The coarseness of the structure in meteorites permitted Young to determine with high accuracy by X-ray reflection from single kamacite lamella the exact orientation of the kamacite lattice with respect to the octahedral plane in the taenite. He found two distinct relations in orientation between the two lattices, both, of course, representing the near identity of the atomic positions in the two planes but differing slightly in angular values. The meaning of this is obscure. A similar study upon

the lattice of the precipitate and the lattice of the parent solid solution. Such a relation, though probably existing, has never been demonstrated for steels; nor has such a relation ever been demonstrated in other systems.

It is clear, therefore, that though numerous examples of the Widmanstätten figure may be discovered in the literature, the only ones for which the plane of precipitation has been demonstrated beyond doubt are the hypoeutectoid steels and the meteorites. And only in the case of the meteorites has a complete analysis been carried through, taking into account the orientation of the lattice in the deposited phase.

Because of the lack of sufficient experimental data no general crystallographic principles governing such cases can now be laid down. The present paper is the first of a series which will attempt, by the study of various Widmanstätten figures, to obtain data pertinent to the general problem.

The Crystallographic Problem

The study of the Widmanstätten figure divides itself naturally into two parts: (1) The crystallographic mechanism operating in precipitation from solid solutions and leading to the formation of the Widmanstätten figure; (2) the factors influencing the growth of the precipitate after the original nuclei have appeared.

Although several Widmanstätten figures have been studied, but two will be discussed here; namely, that formed by precipitation from the δ Al-Ag solid solution and that formed from the α Cu-Si solid solution.

PRECIPITATION FROM FACE-CENTERED CUBIC LATTICES.—CRYSTALLOGRAPHY OF PRECIPITATION IN AL-AG ALLOYS

The aluminum-silver system was chosen for study because in high concentrations of aluminum it was found by Hansen[38] to form excellent Widmanstätten figures upon suitable heat treatment.[39] The ability of

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Widmanstätten figures in ordinary alloys is generally impossible because of the fineness of the structure.

Young also discusses possible movements of atoms in planes parallel to the plane of conversion during the growth of the figure from the original nucleus. This will be discussed later.

[38] M. Hansen: Der Aufbau der aluminiumreichen Silber-Aluminiumlegierungen. *Ztsch. f. Metallk.* (1928) **20**, 217.

[39] Hansen calls these structures simply needlelike and does not point out their striking similarity to Widmanstätten figures in other alloys. As we will see, the deposited phase is not in the form of needles but in the form of plates. This type of structure (as also the martensitic) is almost always described in metallographic literature as needlelike merely because a phase appears on the surface of polish as a needle. Even when the true nature of the structure is recognized the danger of such a loose usage is evident. The Widmanstätten figure in the steels, in meteorites, in this Al-Ag alloy and the martensitic structure, are *not* needle structures but plate structures.

these alloys to form this type of structure rests in the marked change in solid solubility of silver in aluminum with change in temperature (Fig. 3).

The Al-Ag system has been studied by several workers.[40]   For the purposes of the present study the constitution of the system only in the range 0 to 89 weight per cent. silver is important.   The compound AlAg₂ found by Petrenko has been shown by Westgren and Bradley
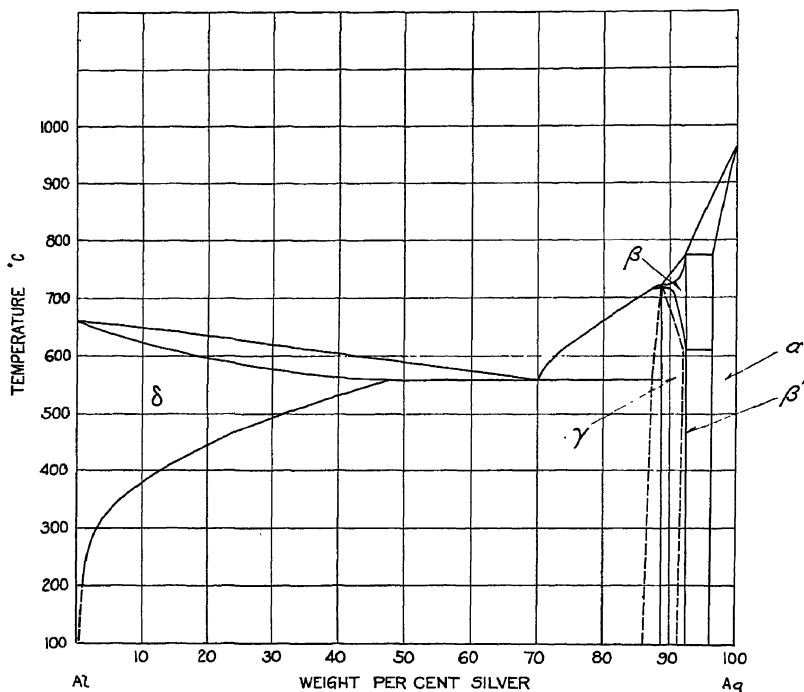

FIG. 3.—CONSTITUTIONAL DIAGRAM FOR AL-AG SYSTEM.

not to be a true intermetallic compound[41] but a typical intermediate solid solution with random distribution of atoms, having a range of homogeneity extending from 86 to 92 weight per cent. silver.

The constitutional diagram given in Fig. 3 is that proposed by Petrenko, modified in the γ range (dotted lines) by Westgren and Bradley.

[40] Thermal analysis: H. Gautier [Sur la fusibilité des alliages métalliques.   Compt. rend. (1896) 123, 109] and G. I. Petrenko [Über Silber-Aluminiumlegierungen. Ztsch. anorg. Chem. (1905) 46, 49]; thermal and metallographic analysis: M. Hansen [Loc. cit.]; electrical conductivity: W. Broniewski [Aluminium-argent.   Ann. chim. phys. (1912) 25, 80]; crystal structure (X-ray): A. F. Westgren and A. J. Bradley [X-ray Analysis of Silver-Aluminum Alloys.   Phil. Mag. (1928) 6, 280].

[41] A. F. Westgren and A. J. Bradley: Loc. cit.

The construction of the diagram in the region of the γ peritectic cannot be correct, as Hansen points out, but for the present purpose the only important point in the constitution of the system is that upon cooling the δ phase precipitates the γ phase.

The Problem.—Since, as we will demonstrate, the γ phase precipitates from the δ in the form of plates, the complete solution of the problem of the crystallographic relations involved in this case consists in a determination of (1) the lattice plane in the δ solid solution upon which the γ phase forms, and (2) the orientation of the lattice of the γ phase with respect to that
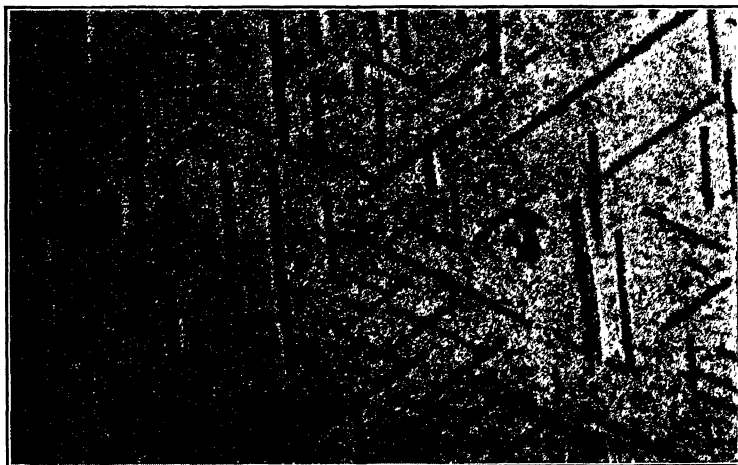
FIG. 4.—LARGE GRAIN IN SILVER-ALUMINUM ALLOY CONTAINING 21.3 PER CENT. AG SHOWING WIDMANSTÄTTEN FIGURE.   × 250.   ETCHED WITH HF.

plane and to the lattice of the original solid solution.   Both of these data have been obtained.

Preparation of Specimens.—An alloy with 21.3 per cent. Ag by weight was prepared and thoroughly homogenized in the δ field.[42]   The alloy was then annealed 17 hr. at 550° to 560° C. and cooled at a uniform rate to 387° C. over a period of 10 hr., then quenched in water.   On polishing and etching this alloy revealed the structure shown in Fig. 4. The precipitated plates of the γ phase are clearly discernable.

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[42] Proof Ag from the U. S. Mint at Philadelphia, and Al analyzing 99.95 per cent. Al were melted in a graphite crucible under a flux of LiCl-KCl.   The Al was melted first and the Ag added to the molten Al.   The alloy was chill cast in an Fe mold, remelted and recast twice.   The ingot was heated to 550° to 560° C. and hammered hot to a 75 per cent. reduction in thickness, and then annealed in flake graphite for 41 hr. at 550° to 560° C. and quenched in water.

Structure of δ Solid Solution

Westgren and Bradley[43] were unaware of the solid solubility of Ag in Al and so made no attempt to study the variation of the side of the unit face-centered cube, a_0, with varying Ag content within the solid solution range.[44]

To determine a_0 on the 21.3 per cent. Ag alloy, filings were heated *in vacuo* at 550° to 560° C. for 19 hr. and quenched in the furnace with water. The filings were immediately washed with alcohol, dried and passed through a 150-mesh screen. These filings were then mixed with filings of the high purity Al used in preparing the alloy and photographed with the familiar General Electric diffraction apparatus. The exposure was complete 3 hr. after the quenching time. No difference in parameter could be detected between the alloy and the pure aluminum. The lines were spotted, but a change in a_0 of 0.1 or 0.2 per cent. should have been clearly evident. Since the alloy is of the age-hardening type the rapidity with which the diffraction photograph is taken after quenching is of importance. No evidence of any γ precipitate could be discovered on the film; so that it is probable that the solid solution had been retained during the exposure time.

In fact, from the identity of the space lattice type (both Al and Ag are face-centered cubic) and the similarity of the atomic volumes (9.98 for Al and 10.27 for Ag) but little change in a_0 would be expected upon solid solution formation of the two elements.

Determination of Plane of Precipitation

The plane in the solid solution lattice upon which the γ phase precipitates was determined in several ways:

1. Fifteen grains exhibiting the Widmanstätten figure in the specimen shown in Fig. 4 were studied. The maximum number of directions of the traces of the precipitated plates upon the plane of polish was found to be four, most grains showing four directions, several showing only three (Fig. 4 shows three).

The significance of this count of directions is that any given lattice plane with Miller index (hkl) will exhibit upon a plane of polish a certain maximum number of directions, corresponding to the number of families of planes with a certain (hkl) index. A few such planes for cubic crystals are listed in Table 1.

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[43] A. F. Westgren and A. J. Bradley: *Loc. cit.*

[44] Their determination of a_0 for the solid solution upon a heterogeneous δ + γ alloy was made upon a slowly cooled alloy and therefore probably referred to a solid solution of less than one weight per cent. of Ag in Al, according to Fig. 3.

TABLE 1.—*Planes for Cubic Crystals*

MILLER INDICES	NUMBER OF FAMILIES OF PLANES[a]	MILLER INDICES	NUMBER OF FAMILIES OF PLANES[a]
100	3	310	12
110	6	311	12
111	4	320	12
210	12	321	24
211	12	410	12
221	12	322	12

[a]Thus for the (111) plane we may have traces upon the surface of polish of the families (111) (11 − 1) (1 − 11) (−111), none of which are parallel. The families of indices (−1 − 1 − 1) (−1 − 11) (−11 − 1) (1 − 1 − 1) are all parallel to the first named in the order given and therefore are identical with them. The (111) plane thus has a maximum of four directions upon a plane of polish.

The occurrence of a maximum of four directions on the plane of polish indicates that the γ phase appears upon the (111) plane. The occurrence of only three directions is easy to understand: it represents a degenerate case of four in which either the plane of polish is nearly parallel to one of the (111) planes which therefore cannot be seen, or two (111) planes intersect the plane of polish so as to give parallel traces.[45]

2. A large single grain showing the Widmanstätten figure was polished on two sides at an angle of about 90°, and the angles of the traces observed on each. Fig. 5 represents one of these polished planes (hereinafter called the first plane), oriented to lie in the plane of the paper and represented stereographically by the full circle. This plane exhibited three directions. The other polished plane, 90° from the first (hereinafter called the second plane), which exhibited four directions, is represented by the full line 0° to 180°. The dashed straight lines represent perpendiculars to the direc-

FIG. 5.—POLISHED PLANE ORIENTED TO LIE IN PLANE OF PAPER. REPRESENTED STEREOGRAPHICALLY BY FULL CIRCLE.

tions of the γ plates on the first polished plane and thus are the loci of normals to all the planes that could have produced these traces. The dashed great circles represent, similarly, the loci of normals to all the planes that could have produced the observed traces on the second plane, 90° from the first.[46]
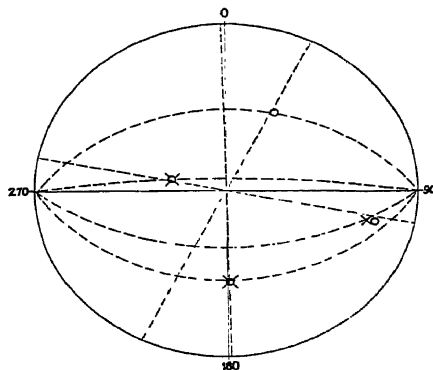
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[45] This method of determining the plane of precipitation is the same as that used by Belaiew (*loc. cit.*, footnote 32) for hypoeutectoid steels.

[46] The method used in plotting these was as follows: A stereographic projection was made with the second secant plane in the plane of the paper, and the straight lines were drawn that gave the loci of the normals to all planes capable of producing the

The intersection of a dashed circle with a dashed line locates the position of a normal to a plane, a plane which can explain a trace on the first secant plane and a trace on the second secant plane simultaneously.

It was readily found, by rotating a stereographic projection of a cubic crystal by means of a stereographic rotation net, that a certain orientation of the (111) planes could be found that would account for these intersections and all the observed traces.[47]   This orientation of the standard cube projection is shown by the small circles in Fig. 2, which are the (111) plane normals.[48]   The solution thus obtained further indicates that one secant plane (the first) will contain but three directions of traces while the other (the second) will contain four, as observed, for on the first secant plane the normals to two of the planes are parallel (at an angle of about 100° in Fig. 5), and the traces of the two planes on the surface will be indistinguishable so far as their directions are concerned.   Although the grain shown in Fig. 4 is not that represented in Fig. 5 it also shows this degeneracy, for the horizontal traces actually represent two planes, and though no difference can be detected in the directions of these traces a difference may be noted in their appearance, certain ones appearing dark and narrow and others light and somewhat broad, a condition brought about by the fact that these two sets of plates are differently tilted with respect to the secant plane.

3. The same grain was deeply etched and mounted on a reflection goniometer.   It was found that the precipitate reflected sharply as fine points of light, clearly distinguishable from the uniform sheen characteristic of the reflection from etch pits in the solid solution.[49]

The action of the etching agent was apparently to throw the γ phase into relief so that the surfaces of the plates acted as reflection surfaces. The use of the reflection goniometer permitted the determination of the orientation of these reflection surfaces with respect to the surface of polish.   Plotted upon Fig. 5 as plane normals these reflections (the crosses) agree very closely with three of the normals to the (111) planes derived

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traces in this secant plane.   With the aid of a 15¾-in. stereographic rotation net graduated to degrees these loci were rotated through 90° and the circles transferred to the stereographic projection of the first face.   As they were planes perpendicular to the paper before rotation, they are seen as great circles after rotation.

[47] The analysis would be simpler if a third face were polished and its data also transferred to this projection.   Then there would be three loci planes intersecting at the positions sought, and no more than two intersecting elsewhere.

[48] The crosses refer to reflections on a reflection goniometer discussed in the next section.

[49] Similar results have been obtained for reflection from nitride plates in Fe-N alloys, which will be reported in a future paper.   In this case also there was no possible confusion with etch pit reflections.

in method 2; the reflection corresponding to the fourth plane was weak and indefinite in position.

The arguments given under methods 1, 2 and 3 are proof of the precipitation of the γ phase upon the (111) plane in the δ phase. It is clear from what has been said that the γ precipitate is in the form of plates. It was observed that the markings of the γ precipitate on two faces cut at any given angle were about equal in length, a condition possible only in the case of a plate structure. All the (111) planes have precipitate upon them, and apparently in equal amounts, though no accurate count of plate traces was made.

Structure of the γ Phase

The structure of the precipitate (the γ phase) is hexagonal close-packed, having the dimensions $a_0 = 2.879$, $c_0 = 4.573$, $\frac{c_0}{a_0} = 1.588$ when saturated with aluminum, and $a_0 = 2.865$, $c_0 = 4.653$, $\frac{c_0}{a_0} = 1.625$ when saturated with silver.[50] It is an intermediate solid solution, not an intermetallic compound as first thought, for the Ag and Al atoms are arranged at random upon the hexagonal close-packed lattice.

Similarities in Structure

The work of Young on meteorites[51] suggests that the mechanism of the formation of the Widmanstätten figure is a transformation of a lattice plane in the parent solid solution into a closely similar plane in the precipitate. The first step is therefore to look for closely similar planes in the two participating structures. These two participating structures are here the δ solid solution, with a space lattice indistinguishable from that of pure Al, and the γ solid solution. Table 2 lists several of the smallest interatomic distances in the two phases.

In looking for similarities in the two structures one is struck by the near equality of the smallest interatomic distance in Al (2.858Å) and the two shortest distances in the γ lattice, 2.827 and 2.879Å. One of the atom planes in Al containing this shortest distance is the (111), having a hexagonal array of atoms, each atom 2.858 Å. from its neighbors. The basal plane in the hexagonal lattice is almost the same, having also a hexagonal array of atoms, each atom 2.879 Å. from its neighbors. Thus an enlargement of less than 2 per cent. changes the array of atoms upon the (111) plane in Al into the array of atoms (with a different ratio of Al and Ag atoms) upon the (00.1) plane in the γ phase. The only other low indices planes that resemble each other are the (110) and (11.0) the former having atoms at the corners of rectangles whose sides are 2.858 and

[50] A. F. Westgren and A. J. Bradley: *Loc. cit.*
[51] J. Young: *Loc. cit.*

TABLE 2.—*Interatomic Distances*

δ Lattice		γ Lattice	
Atom Position	Distance from Atom at 0, 0, 0, Ångstroms	Atom Position[a]	Distance from Atom at 0, 0, 0, Ångstroms
½, ½, 0	2.858	⅔, ⅓, ½	2.827
1, 0, 0	4.042	1, 0, 0	2.879
½, ½, 1	4.951	0, 0, 1	4.573
1, 1, 0	5.716	2, 1, 0	4.987
1, 1, 1	7.001	1, 0, 1	5.422
		1, 1, 1	6.765

[a] Referred to hexagonal axes at 120°.

4.042, the latter having atoms at the corners of rectangles whose sides are 2.879 and 4.573.

The interplanar distances are of interest, and are tabulated in Table 3.

TABLE 3.—*Interplanar Distances*

Aluminum		Precipitate	
Plane	Interplanar Distance	Plane	Interplanar Distance
(111)	2.333	(00.1)	2.286
(110)	1.429	(11.0)	1.662
			0.831

Here again there is a close similarity between the (111) and (00.1) planes, while there is a considerable difference between the (110) and 11.0) planes.

The distribution of atoms in space will now be considered. The axial ratio of the hexagonal close-packed gamma phase saturated with aluminum is 1.625, which is close to the value for the closest packing of spheres, 1.633. Spheres can be close-packed in an infinite number of ways, the two simplest (and the only ones in which the atoms are all equivalent) being hexagonal close-packed (when the axial ratio is 1.633) and face-centered cubic. The difference between the spatial distribution of atoms in these two packings is not great. Referred to hexagonal axes X, Y, Z at 120°, consider three layers (A), (B), (C), of atoms each having an hexagonal close packing of atoms with (A) an atom at $X = 0$, $Y = 0$, (B) an atom at $X = ⅔$, $Y = ⅓$, (C) an atom at $X = 4/3$, $Y = ⅔$. These layers are then superimposed with their origins directly above each other, in the sequence ABCABC . . . to give the face-centered cubic type of packing, and in the sequence ABABAB . . . to give the hexagonal close packing. It will be seen that the transformation of ABCABC . . . into ABABAB . . . requires simply that the third and fourth

layers of the former be shifted equally, the fifth and sixth layers be shifted equally, the seventh and eighth like the first and second remain as they were, and so on. The amount of the shift is in each case the distance between neighboring "hollows" of the layers of spheres. If the face-centered aluminum transforms into the gamma phase by this shifting, (111) planes become (00.1) planes parallel to them. Furthermore, these two parallel planes ((111) and (00.1)) will be orientated with respect to each other so that the (11.0) direction in the (00.1) plane is parallel to the (110) direction in the (110) plane.

In Table 4 are given the number of atoms at different (small) distances from an atom of a hexagonal *surface layer* (A) for the aluminum lattice and the aluminum-saturated gamma lattice. The similarity is striking.

TABLE 4.—*Distances of Atoms from Atom in Surface Layer*

Layer	Number of Atoms	Distance 10^{-8} Cm.	
		Aluminum	Precipitate
A	6	2.858	2.879
B	3	2.858	2.826
B	3	4.041	4.031
C	1		4.572
C	3	4.950	
A	6	4.948	4.984
A	6	5.716	5.758

Suggested Mechanism of Precipitation

From this standpoint it seems not unreasonable to suggest that the process of precipitation upon decreasing solubility by lowering temperature is, first, a diffusion of silver atoms into a region in sufficient numbers to make the aluminum solid solution in this region unstable, and second, a shifting of certain (111) planes of this solid solution over the adjacent planes into positions of lower potential energy, as described above.

Whether or not the precipitate orientates itself as suggested because the total potential energy of the lattices is less with this orientation than with any other need not be discussed at length in this case, for it would appear necessary only that the postulated orientation be *one* of those having minimum energy. The influence of the solid solution lattice should tend to force the precipitate to take this orientation *regardless of other possible orientations of low energy*. The extent of the precipitate lattice on a (111) plane should be in two dimensions rather than one; that is, one would not expect to find the growth of the precipitate (00.1) plane to be much greater in one direction than in another. Possibly in

the ideal case of very slow growth in highly pure alloys the precipitate crystals would be hexagonal prisms.

From the above considerations we might, then, expect not only th (00.1) plane in the precipitate to be parallel to the (111) plane in the soli solution, but also the (11.0) direction in the (00.1) plane of the precipitai to be parallel to the (110) direction in the (111) plane of the solid solutioi The experiments about to be described confirm these predictions.

Determination of Orientation of Precipitated Lattice

Young's solution of a similar problem in the meteorites[52] was relativel simple, since the kamacite precipitate is of sufficient size to permit a X-ray determination of the orientation of any one kamacite lamella. I the present case, however, the precipitate occurs in a very fine form and technique parallel to that used by Young was out of the question.

The problem was attacked in a different way. A rod of the 21.3 pe cent. Ag alloy, 3 mm. in diameter, was drawn in steel dies to 0.63 mn immediately after it had been annealed 48 hr. at 550° to 560° C. an quenched in water. The wires were then heated 24 to 150 hr. at 100' 200° and 350° C.

The object of this treatment was to produce a fiber structure in th homogeneous δ solid solution by wire drawing and subsequently to induc the precipitation of the γ phase by reheating to moderate temperature. It was found by Dahl, Holm and Masing[53] that an alpha Cu-Be allo treated in this way exhibited not only a fiber structure in the face-centere cubic alpha solid solution, but also a fiber structure in the body-centere copper-beryllium intermetallic compound which precipitated on annealin; The fiber structure in the precipitate could not have been induced by th process of wire drawing, since presumably it did not appear until the wir had been annealed, and since it is highly unlikely that the process of sli in a highly brittle intermetallic compound should obtain to such a degre as to give well marked fibering. The obvious explanation of the fiberin of the precipitate is that it was produced by the Widmanstätten mechar ism, with a definite crystallographic relation between the present soli solution and the precipitate, in a solid solution which had a preferre orientation and thus took its fiber structure from that of the parent soli solution. A study of the relation of the two fiber structures should the afford a solution for the orientation of the precipitate lattice with respec to the parent solid solution lattice.

After the annealing treatment diffraction photographs were take with filtered Mo-K radiation (30,000 volts). These showed incon

[52] J. Young: Loc. cit.
[53] O. Dahl, E. Holm and G. Masing: Wiss. Veröffentlich. Siemens-Konzei (1929) 8, 154–185.

plete fibering.[54]   Those annealed for long periods at 350° showed some recrystallization, those annealed at 100° showed no precipitation.   The best photographs were obtained with 24 to 50 hr. at 350°.   After the wires had been reduced to 0.2 or 0.3 mm. by etching in dilute hydrochloric acid, the fibering was intense and nearly perfect.   Figs. 6 and 7 are the X-ray diagrams obtained with the beam at 90° and 50° to the axes of the wires.   By overexposing the spots due to the solid solution, the spots due to the precipitate were readily seen.

FIGS. 6 AND 7.—X-RAY DIAGRAMS OBTAINED WITH BEAM AT 90° AND 50° TO AXES OF WIRES.

The fiber structure of the solid solution of silver in aluminum proved to be the same as that of aluminum.   A stereographic projection of the (111) and (110) planes of one of the aluminum grains in such a structure is shown in Fig. 8.   (The direction of the wire or fiber axis in this and the succeeding figures is indicated by *F-F*.)   The standard projection of low index planes of the precipitate lattice is given in Fig. 9.   By rotating the latter on a 15¾ in., one-degree rotation net the positions of these planes were plotted for the assumed orientation of the precipitate on the (111) planes; *i. e.*, with (00.1) plane parallel to the (111) and the (11.0) direction

[54] Wires have a zoned structure with regard to the degree of preferred orientation of grains.   E. Schmid and G. Wasserman: Über die Textur hartgezogener Drähte. *Ztsch. f. Phys.* (1927) **42,** 779.

parallel to the (110). Fig. 10 plotted in this manner gives the projection of all the precipitate planes that give the strongest reflections to be found
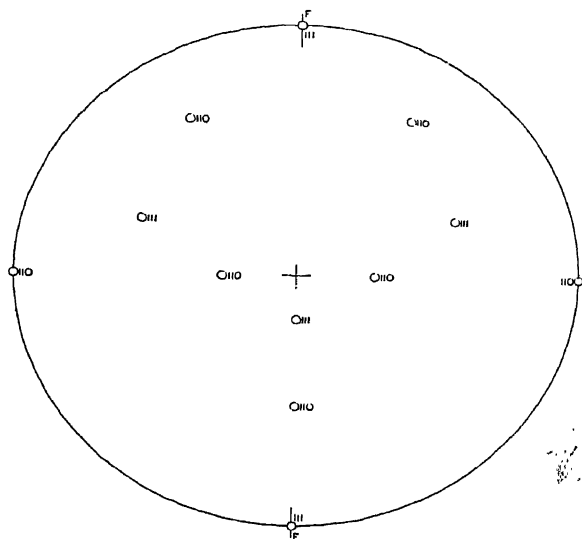
FIG. 8.—STEREOGRAPHIC PROJECTION OF (111) AND (110) PLANES OF ALUMINUM GRAIN IN FIBER STRUCTURE OF AG-AL SOLID SOLUTION.
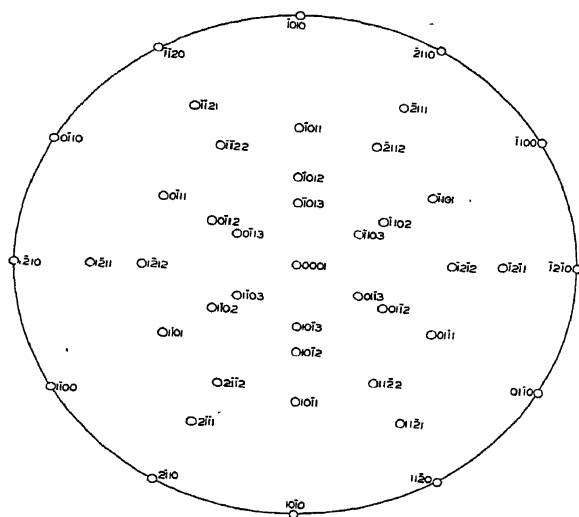
FIG. 9.—STANDARD PROJECTION OF LOW INDEX PLANES OF PRECIPITATE LATTICE.

in Fig. 6 (the normal to any one of these planes cuts the projection sphere in two points, only one of which is shown in the figure). The stereographic projection of a wire with perfect fibering is obtained from Fig. 10

by rotating it about the axis *F-F*. Then the parallels of latitude passing through the plane normals represent the combined projections of all possible positions of the planes in the polycrystalline wire. (Both intersections of the normals with the sphere of projection should now be con-
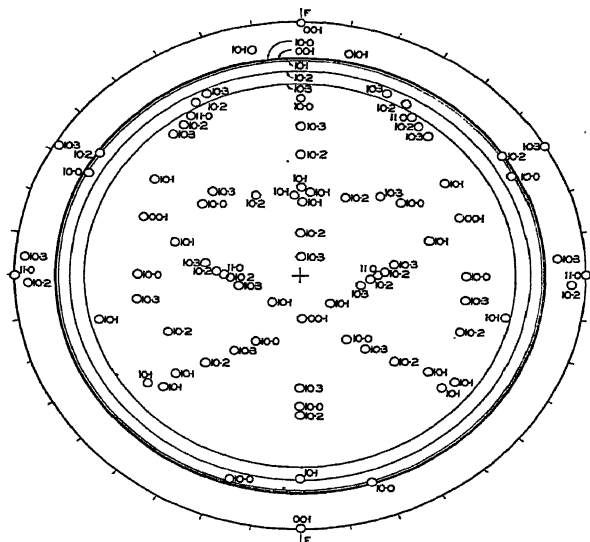
FIG. 10.—PROJECTION OF PRECIPITATE PLANES THAT GIVE STRONGEST REFLECTIONS TO BE FOUND IN FIG. 6.

sidered, giving the diagram symmetry about a horizontal axis.) Only those planes that are in the position for which

$$n\lambda = 2D \sin \theta$$

will reflect; they are located by drawing "reflection circles" on the sphere about the X-ray beam at angles $90 - \theta°$ from it.[55] The intersection of the reflection circles with the parallels of latitude through the corresponding planes are then the positions of the reflection planes, and the angles of these planes from the vertical axis are the same angles at which the spots due to them will be found on a film placed perpendicular to the X-ray beam behind the wire. The circles in Fig. 10 are the reflection circles for the planes contributing to the actual diagrams obtained (with the X-ray beam perpendicular to *F-F*), and the crosses in Fig. 11 are the calculated positions of spots on the film. (The positions of the Al spots were taken from the literature.)

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[55] M. Polanyi: Das Röntgen-Faserdiagramm. *Ztsch. f. Phys.* (1921) **7**, 149.

v. Göler und G. Sachs: Walz und Rekrystallisationstextur regularflächenzentrierter Metalle. *Ztsch. f. Phys.* (1927) **41**, 873.

One of the films obtained with this arrangement is reproduced in Fig. 6 and the spots from two films are plotted as open circles and dots in Fig. 11. Agreement in position of calculated and observed spots is satisfactory, though the accuracy is not high. Agreement of intensities is also satisfactory; the two spots predicted and not found are calculated to be of low intensity, and the strongest spot due to the precipitate is shown by the graphical analysis to be strong because of wide contact between the reflection circle and the corresponding plane normal circle, with consequent large numbers of planes in position to reflect.
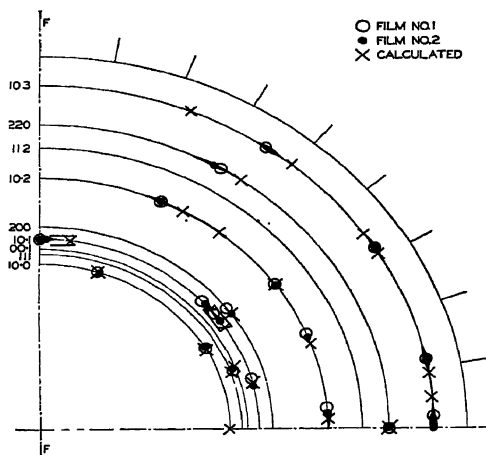
FIG. 11.—SPOTS FROM TWO X-RAY FILMS.

TABLE 5.—*Values of α from Fig. 10 and Observed Values from Fig. 7 Read by Aid of Bozorth's Chart*

Plane	Radius of Debye-Scherrer Ring on Film at 4 Cm. Distance	α Predicted	α Observed	Remarks
(111)	1.11	70° 32'	70°	Mo.K$_\beta$ radiation[a]
(10.0)		20°		Not reflecting
		62°	61°	
	1.18	90°	90°	
(111)	1.26	70° 32'	70°	
(00.1)	1.29	0°		Not reflecting. Falls
		70°		on (111) spot
(10.1)	1.36	53°–59°	50°–65°	
		77°	75°	
(200)	1.46	54° 44'	55°	
(10.2)	1.80	32°	28°–30°	
		39°		
		55°	58°	
		70°	67°	
		89°	87°	
(220)	2.19	35° 15'	36°	
		90°	90°	
(10.3)	2.46	28°	30°	
		43°	41°	
		58°	59°	
		81°	78°	
		85°	86°–90°	

[a] All other reflections are due to Mo.K$_\alpha$ rays.

Another test of the assumptions was made by taking photographs with the wire axis inclined 50° to the beam, the film remaining perpendicular to the beam (reproduced in Fig. 7). A solution of this film could also have been obtained stereographically, but an easier method is that of Bozorth [56] The angular distance of the parallels of latitude from the *F-F* axis is α in Bozorth's notation.

Table 5 gives the values of α read from Fig. 10 and the observed values read from the film of Fig. 7 by placing a suitably enlarged Bozorth 50° chart over it. The agreement is such as to leave no doubt as to the correctness of the assumptions involved.

Conclusion Regarding Al-Ag Precipitation

It has been demonstrated, therefore, that the γ phase in the Al-Ag system precipitates in the form of plates from the δ solid solution upon cooling. These plates are parallel to the (111) planes, the octahedral, in the face-centered cubic lattice of the δ phase. The γ phase is oriented upon these (111) planes in such a way that the basal plane (00.1) is parallel to the (111) plane in the δ phase and in such a way that analogous directions on the two planes are parallel since the (11.0) direction upon the (00.1) plane is parallel to the (110) direction upon the (111) plane.

CRYSTALLOGRAPHY OF PRECIPITATION IN CU-SI ALLOYS

Copper-rich copper-silicon alloys have been studied by a number of investigators. For the present purpose the only interest is in the solid-solubility curve bounding the α phase and in the nature of the phase which on cooling precipitates from the α solid solution.

The course of the solid-solubility curve bounding the α phase has been studied by Corson[57] and more completely by Smith.[58] The construction given by Smith for this part of the *t-x* diagram is shown in Fig. 12. Obviously alloys between 4 and 6.7 per cent. Si by weight fulfill the conditions enumerated above (represented graphically in Fig. 2) for the formation of the Widmanstätten figure. In fact, several of the photomicrographs given by Smith suggest the figure, notably his Figs. 11 and 12.

[56] R. M. Bozorth: Orientation of Crystals in Electrodeposited Metals. *Phys. Rev.* (1925) **26**, 390.

[57] M. Corson: Copper Alloy Systems with Variable Alpha Range. *Proc.* Inst. Met. Div., A. I. M. E. (1927) **1**, 435.

[58] C. S. Smith: The Alpha-phase Boundary of the Copper-silicon System. *Jnl.* Inst. Metals (1928) **40**, 359; Constitution of the Copper-silicon System. *Trans.* A. I. M. E., Inst. Met. Div. (1929) 414. The present nomenclature of phases is taken from the latter paper.

It seems likely, from an inspection of Smith's photomicrographs, that the γ phase precipitating from the α phase in the concentration range 4 to 6.7 per cent. Si takes the form of plates. It is not possible, however, to tell from Smith's photomicrographs what the maximum number of directions exhibited by the plates on the plane of polish may be, though there is a suggestion that the number is higher than that corresponding to a plane of low indices (Table 1).
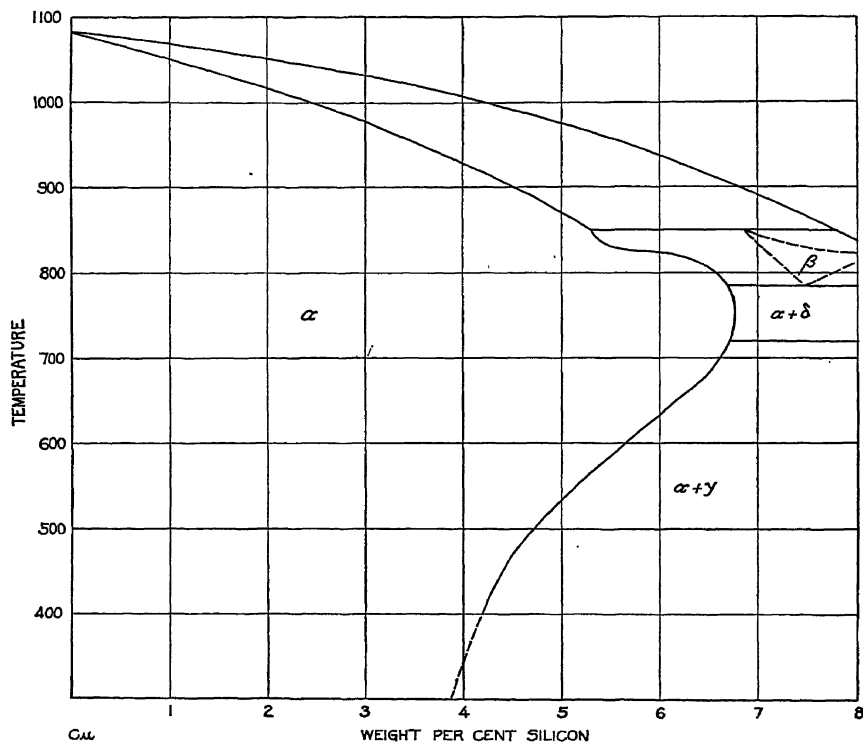

FIG. 12.—CONSTITUTIONAL DIAGRAM OF CU-SI SYSTEM.

If the γ phase should precipitate on a crystallographic plane other than the (111) plane, it is clear that Osmond and Cartaud's proposed generalization cannot be maintained. In order to make an immediate test of Osmond and Cartaud's proposal it was thought desirable to study this precipitation. The results reported below are incomplete, for it was not possible to identify the plane of precipitation. Enough data have been obtained, however, to demonstrate that the plane of precipitation cannot be the (111) plane. It is felt that these results should be presented immediately because of their theoretical bearing.

Experimental Procedure

An alloy of copper and silicon was prepared from electrolytic copper cut directly from the cathode and silicon analyzing 0.56 per cent. Fe, 0.58 Al, 0.05 Cu, 0.075 Cr. and remainder Si. Weighed portions of the two elements were melted together in a graphite crucible under vacuum by induction heating. The resultant ingot was remelted in air under molten sodium chloride and chill-cast in a steel mold into square bars 1 in. in section. These bars were heated under graphite at a temperature of 780° C. for four days, then quenched in cold water. The final alloy analyzed 6.00 per cent. Si.

No success was to be had in developing a well formed Widmanstätten figure by controlled rates of cooling. It was necessary to quench and

FIG. 13.—LARGE GRAIN IN COPPER-SILICON ALLOY CONTAINING 6.0 PER CENT. SI, SHOWING WIDMANSTÄTTEN FIGURE. × 220. ETCHED WITH $NH_4OH + H_2O_2$.

reheat to moderate temperatures in order to develop the γ plates sufficiently well so that the angles they made in the plane of polish could be measured satisfactorily.

A sufficiently well defined structure could be developed by reheating the quenched alloy to 350° for 10 hr. Fig. 13 shows a photomicrograph of one large grain in a piece treated in this way.

It has been found, by work on other alloys exhibiting a structure similar to that shown in Fig. 13, that the plane of precipitation can be discovered by determining the orientation of the solid solution matrix and demonstrating upon a stereographic projection of this orientation that the traces of the plates upon the plane of polish may be explained by one, and only one, crystallographic plane in the solid solution matrix. An attempt was made to solve the present problem in this way, but it was

impossible to get sufficiently strong X-ray reflections from the distorted α solid solution matrix, so that the orientation of the α solid solution matrix could not be determined.[59]

It seemed sufficient for the present purpose merely to demonstrate that the plane of precipitation cannot be the (111) plane. A complete solution of the problem exhibited by the 6 per cent. alloy would require that the crystal structure of the precipitate be known and the orientation of the precipitate with respect to the plane of precipitation be determined, as was done in the aluminum-rich Al-Ag alloys. The structure of the γ phase, however, is unknown and an attempt at a complete solution must await its determination.

Table 1 shows the number of families of planes accounted for by crystallographic planes of given Miller indices. These numbers represent the maximum number of directions that any crystallographic plane may exhibit as lines upon the plane of polish. If it be found that the maximum number of directions exhibited by plates upon the plane of polish is 12, the problem will not be solved, since a large number of crystallographic planes show 12 families. In this case, however, there can be no doubt that the crystallographic planes of lower indices are excluded, for no plane or combination of planes of lower indices will account for 12 directions on the plane of polish.
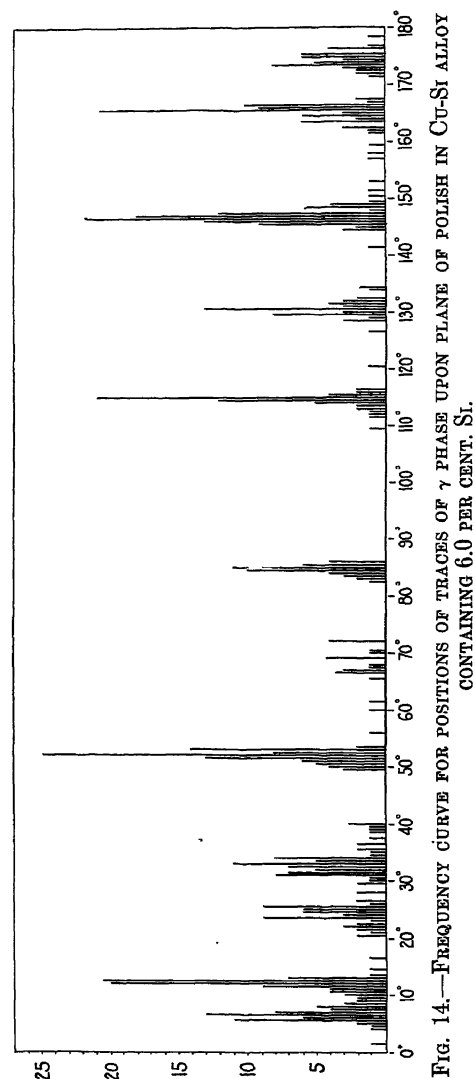
FIG. 14.—FREQUENCY CURVE FOR POSITIONS OF TRACES OF γ PHASE UPON PLANE OF POLISH IN CU-SI ALLOY CONTAINING 6.0 PER CENT. SI.

The angles formed by the traces of the γ phase with respect to an edge upon the plane of polish of the grain shown in Fig. 14 were measured by a protractor to 0.1°. In all, 699 traces were measured and arbitrarily arranged into 0.5° groups. The angles determined are plotted in Fig. 14 as abscissas. The ordinates represent the number of traces at any given half-degree angle. Fig. 14, therefore, is an experimental frequency curve.

There are 12 well defined maxima upon this graph. There is an unavoidable scattering of the angles, resulting doubtless from imperfections in the plates themselves and also from imperfections in the edges of the plates left by the polishing operation, but the prominence of the maxima leave little doubt of the validity of these 12 directions. The most likely angular values may be read from the graph as 6.0°, 13.5°, 24.0°, 33.0°, 52.0°, 69.0°, 84.5°, 114.5°, 130.5°, 146.5°, 165.5°, 174.5°.

Conclusion Regarding Cu-Si Precipitation

It seems certain, therefore, that the precipitation of the γ phase from the α solid solution in the Cu-Si system cannot be upon the densest packed plane, the (111) plane, but must be upon some crystallographic plane displaying 12 families of crystallographic equivalent planes.

DISCUSSION OF RESULTS

Most of the necessary discussion has been included in the body of the text and need not be repeated here. The essential theoretical aspects of the problem, however, might be profitably recapitulated, and for this purpose it should be useful to summarize and appraise the data available.

It may be said immediately that the sole generalization heretofore available cannot be correct. Osmond and Cartaud's proposal that the precipitates should seek the crystallographic plane of greatest atomic density ("reticular density") though met by the precipitation of ferrite from austenite in Fe-C alloys, of kamacite from taenite in Fe-Ni alloys (meteorites), and of the γ phase from the δ in Al-Ag alloys, is definitely denied by the precipitation of the γ phase from the α phase in Cu-Si alloys, which is upon a plane of 12 families whereas the densest plane is the (111) with but four families, and also by the precipitation of the iron nitride from the solid solution of nitrogen in α iron,[60] which is upon the (210) plane in the α iron, eighth in order of densest atomic packing.

Nor does there appear to be any relationship between the plane of precipitation and the cleavage plane, for there is no evidence of cleavage in α iron upon the (210) plane [the plane of cleavage in α iron is (100)] nor in copper-rich α solid solutions (Cu-Si) upon a plane with 12 families.

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[60] A preliminary report of the study of Fe-N alloys was published by the present authors [Some Observations upon the System Iron-Nitrogen. *Metals and Alloys* (1930) **1**, 442–433]. A complete account of this work will be presented later.

The term "cleavage plane precipitation" thus seems to be meaningless, though it has been used frequently.

In forming any theory of the formation of the Widmanstätten figure an adequate body of experimental data should first be produced. It is the intention of the present series of papers partially at least to accomplish this. It should help, however, in developing such a theory to discuss at the present time possible meanings of the information now at hand. The data now available are these:

1. The body-centered cubic kamacite precipitated from the face-centered cubic taenite in Fe-Ni alloys takes the form of plates which are parallel to the octahedral or (111) planes in the face-centered cubic taenite.

2. The lattice of the kamacite is so oriented upon these (111) planes that one of its (110) planes is parallel to the (111) plane in the taenite, with analogous directions on the two conjugate planes parallel.

3. The body-centered cubic ferrite precipitated from the face-centered cubic austenite in hypoeutectoid Fe-C alloys takes the form of plates which are parallel to the octahedral or (111) planes in the face-centered cubic austenite. No further data are available for these alloys.

4. The hexagonal close-packed γ phase precipitated from the face-centered cubic δ phase in Al-Ag alloys precipitates in the form of plates parallel to the (111) planes in the face-centered cubic δ phase.

5. The lattice of the phase is so oriented upon these (111) planes that its basal plane (00.1) is parallel to the (111) plane, with analogous directions on the two conjugate planes parallel.

6. The γ phase precipitated from the face-centered cubic α phase in the Cu-Si alloys is in the form of plates parallel to some crystallographic plane forming 12 families of equivalent planes.

7. The iron nitride precipitating from the solid solution of nitrogen in body-centered cubic α iron is in the form of plates parallel to the (210) plane in the α iron lattice.

8. The precipitate from a solid solution does not always take the form of plates but may exhibit a variety of forms.[61]

The suggestion is strong, even from this limited evidence, that the lattice of the parent solid solution is not the only controlling factor, for if this were the case the γ phase should form upon the (111) plane in the face-centered cubic α phase in the Cu-Si alloys, since this plane was sought by the precipitate in forming from the face-centered cubic phase in the Fe-Ni, Fe-C and Al-Ag alloys.

The relationship in orientation between the lattice of the precipitate and that of the solid solution in the Fe-Ni alloys, demonstrated by Young,

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[61] Work at present underway has shown that in some alloys true needles may form by precipitation from solid solution, whereas in other cases other geometrical forms may be taken by the precipitate. In every case the position of these forms of the precipitate is governed by the orientation of the present solid solution lattice.

and in the Al-Ag alloys, demonstrated by the present authors, strongly suggests that the true mechanism of the formation of the Widmanstätten figure must be sought in a cooperation between the lattice of the precipitate and the lattice of the parent solid solution.

To make the process graphic, let us develop a picture of the atomic changes, admitting it to be purely tentative and for the moment restricted
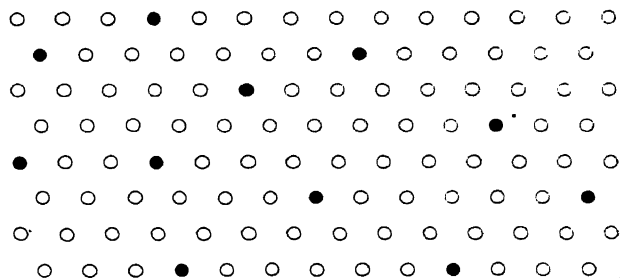

FIG. 15.—ARRANGEMENT OF ATOMS ON THE (111) PLANE IN 10 PER CENT. NI ALLOY.
Black atoms are those of nickel, the others are iron.

to the formation of plates. Young pointed out that the close similarity in the atomic arrangement and the interatomic distances between the (111) plane in taenite and the (110) plane in kamacite could be advanced as a reason for the formation of plates, since upon cooling at the temperature of beginning precipitation of kamacite a "ready-made" plane was available in the taenite [the (111)] for the formation of a plane [the (110)]
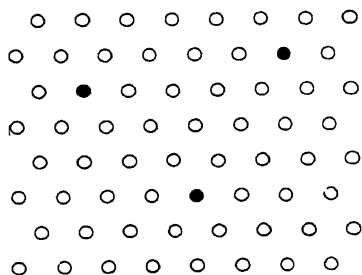
FIG. 16.   FIG. 17.

FIG. 16.—ARRANGEMENT OF ATOMS ON (111) PLANE IN 10 PER CENT. NI ALLOY AT MOMENT OF PRECIPITATION.
FIG. 17.—ARRANGEMENT OF ATOMS ON (110) PLANE IN 10 PER CENT. NI ALLOY JUST AFTER PRECIPITATION.
Black atoms are those of nickel, the others are iron.
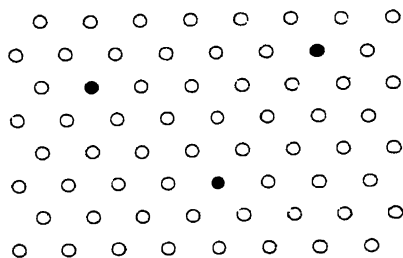
in kamacite. With this as a starting point let us attempt to write a history of the process of precipitation.

Fig. 15 shows a (111) plane in taenite in an Fe-Ni alloy with 10 atomic per cent. of nickel. These atoms must be considered in continual motion

from point to point on the lattice; that is, there is an internal diffusion within the grain. Such an atomic motion of the solute must be random with localized surges of high concentration of either iron or nickel atoms. As the alloy cools and impinges upon the transformation curve (Fig. 2) conditions of stability demand the appearance of the kamacite phase, with approximately 5 atomic per cent. Ni. With the postulated surges in concentration in the taenite lattice there will occur from time to time minute areas upon the (111) plane (or any other) with correct concentration of iron and nickel to form the kamacite phase with 5 atomic per cent. Ni, as shown in Fig. 16. At the precipitation temperature these areas upon the (111) plane transform by alteration in interatomic distances to configurations bearing the geometry of the kamacite phase, as shown in Fig. 17. These new transformed areas are thus nuclei for the formation of kamacite. Since the distribution of the minute areas in the taenite must be random, originating in chance surges in concentration, the distribution of the transformed areas likewise will be random (in the absence of disturbing factors) and the resulting duplex alloy will show a uniform or random distribution of the kamacite phase.

These postulated surges in concentration must occur, of course, on all lattice planes, but there is no other lattice plane in taenite so nearly similar to a lattice plane in kamacite as the (111) plane. The configuration in Fig. 16 is thus almost identical to that in Fig. 17. The preference for the (111) plane thus lies in the near identity of the two conjugate planes. The transformation occurring on any other pair of conjugate planes would involve a relatively much greater atom shift.

If this theory is correct the plane of precipitation could not be predicted from the type of space lattice of the parent solid solution. In fact, two different crystal forms precipitating from the same solid solution might well seek different planes. Upon this basis a tentative hypothesis might be advanced:

When a phase forming by precipitation from a solid solution takes the form of plates, the lattice plane on which the new phase forms is that upon which the atoms are nearly identical in position and interatomic distance to some plane in the precipitate lattice.

Young pointed out that the plane of precipitation in taenite, the (111), is the densest packed in the taenite lattice, and that the plane in kamacite parallel and coincident with it, the (110), is the densest packed in the kamacite lattice. The essential difference between the previous views, including that of Young and those enunciated here, lies in the fact that it is no longer held that the density of atomic packing on the conjugate planes is of first importance, for planes of relatively low atomic density may be sought for precipitation when there is a close agreement in atomic arrangement and interatomic distances between it and some phase in the precipitate.

This hypothesis is built entirely upon the assumption of plate formation. In cases where the Widmanstätten figure is constituted of other geometrical forms, such as true needles, the hypothesis would have to be modified. It is possible that the formation of true needles may be conditioned by a near equivalence of conjugate *directions* in the parent solid solution lattice and the lattice of the precipitate and a lack of near equivalence on lattice planes. A theoretical discussion of such cases must be deferred until sufficient experimental data can be made available.

The picture outlined above describes only the formation of the original nuclei, and must be amplified to include the process of growth of these nuclei into discrete grains.

It is easy to understand that the growth velocity should be greater upon the plane of precipitation in the solid solution lattice than upon any other, for, to use Young's term, the plane of precipitation is "ready-made" for a plane in the precipitate. Growth along the plane of precipitation must result in an impoverishment of one of the constituents along this plane, with the result that the regions lying on either side of the plate must become more effective in precipitation.

The building up of the precipitate in a direction perpendicular to the plane of precipitation has been discussed by Young for meteorites, and previously in this paper for an Al-Ag alloy. If the two planes participating in the precipitation—the plane in the parent solid solution lattice and the plane in the lattice of the precipitate coincident with it—are nearly identical, it may be seen immediately that lying behind the two planes are similar planes bearing the same relation. Each of the two respective lattices may be considered as built up entirely of these two types of planes.

A slight shift in atomic positions on all the planes of one type will render them nearly indistinguishable from the planes of the other type. For a complete transition from the first type of lattice to the second, in general these transformed lattice planes would have to shift in relation to one another to fulfill the requirements of symmetry of the new lattice; that is, a shearing of lattice planes would be necessary.

Thus, for the transformation of the lattice lying behind the original nucleus two processes would have to be operative; namely, a shifting or shearing of atom planes and a transformation of the shifted planes into the new planes, as represented in Figs. 16 and 17. Whether or not this is the true mechanism of growth cannot now be said. The authors are inclined to believe that the necessity for growth perpendicular to the plate originates in an impoverishment of the plane of precipitation in one type of atom with concomitant more effective growth velocity perpendicular to the plane, and that the mechanism of this growth may either be atomic —that is, the growth taking place atom by atom—or planar, as described above.

Doubtless it will be remarked that the theoretical viewpoints expressed in this paper are built upon lattice geometry with but little reference to lattice energetics, especially interfacial energies.   With a body of experimental data larger than that now available, an analysis of the energetics of the Widmanstätten mechanism would be desirable but in the present state of knowledge such an analysis would be too formal to be of real value.

SUMMARY

1. Previous studies on the structures originating in a precipitation from a solid solution—Widmanstätten structures and figures—have been reviewed and critically discussed, particularly from the theoretical point of view.   The object of the present study is an understanding of the mechanism of formation of segregates from solid solutions.

2. The precipitation of the γ phase from the δ solid solution in the Al-Ag system has been subjected to experimental study, and it has been found that the γ phase forms plates parallel to the (111) or octahedral planes in the original face-centered cubic δ solid solution.   By a suitable study of fiber structures in the drawn and subsequently heat-treated δ solid solution it has been shown that the basal plane (00.1) in the hexagonal γ phase forms parallel to the octahedral plane (111) in the face-centered cubic δ phase.

3. A study of the precipitation of the γ phase from the α Cu-Si solid solution has been made.   It was found that this phase precipitates in the form of plates parallel to some crystallographic plane in the face-centered cubic α solid solution possessing 12 families of crystallographic equivalent planes.   Although this plane was not identified, it is shown that it cannot be the plane of densest atomic packing, which is the (111) plane.   The significance of this with respect to a previous generalization by Osmond and Cartaud is pointed out.

4. It is suggested that the Widmanstätten figure need not always consist of plates, for true needles and other forms sometimes occur. In every case, however, the orientation of these forms is controlled in part by the orientation of the parent solid solution lattice.

5. It is tentatively proposed that a new phase appearing by precipitation from a solid solution does so in such a way that some crystallographic feature in the lattice of the precipitate forms directly with a minimum shift of atoms from a nearly identical crystallographic feature in the parent solid solution lattice.   Such a theory does not require that the new phase appear as plates parallel to the plane of densest atomic packing in the original solid solution lattice and is in better accord with the experimental data here presented than previous theories.

A picture of the atomic kinetics of such a process is presented.

DISCUSSION

(S. L. Hoyt presiding)

A. SAUVEUR, Cambridge, Mass. (written discussion).—The authors have thrown a great deal of light on the mechanism of the formation of the Widmanstätten structure, a question of fundamental importance in the study of the constitution of alloys. With one or two unimportant exceptions, I find myself in complete agreement with the conclusions drawn from the results of their skillfully conducted experiments, fully realizing that they are based on an intimate and accurate knowledge of the meaning of lattice structures as revealed by X-ray diffraction spectra—a knowledge possessed by relatively few. Of special interest to me is the authors' discussion of the structure of martensitic steel. I share their belief that in retarding by quenching the transformation of austenite until a temperature of some 300° C. is reached, the new alpha phase, called by many "martensitic needles," form, along some slip planes (octahedral) resulting from the change of volume accompanying the allotropic transformation. Were it possible to quench steel without causing slip planes, it is not likely that austenite would transform at all. In other words, at some 300° C. austenite, although decidedly in an unstable and undercooled condition, would not transform were it not for the formation of slip planes. We are tempted to generalize and to state that the production of slips, whether by quenching or by cold working, promotes the return of an unstable condition to a more stable condition. Witness the formation of alpha iron in Hadfield manganese steel after severe cold working, or the production of over 90 per cent. of alpha iron in 18–8 austenitic steel by cold working alone.[62] We infer from these phenomena that neither Hadfield manganese steel nor 18–8 steel are truly stable from a physicochemical standpoint. If they were truly stable, the production of slip planes would not induce the formation of some alpha phase, necessarily accompanied by the reappearance of ferromanganese.

I disagree with the authors in their belief that a Widmanstätten structure is promoted in hypoeutectoid steel by fast cooling through the thermal critical range sometimes called "secondary crystallization." An extensive series of experiments conducted in my laboratories by Dr. Chou has shown to our satisfaction that the reverse is true. Fast cooling permits only a limited separation of the new constituent along the boundaries of the gamma grains, giving rise to what is familiarly described as a network structure, the grains themselves being of a sorbitic nature rather than pearlitic. Slow cooling, on the contrary, affords the time necessary for a full rejection of the alpha constituent (ferrite) not only on the outside of the grains but within each grain and along the 111 planes of the parent austenite. Evidences to that effect have been presented in a recent paper by Dr. Chou and myself.[63]

I do not quite understand the authors' hesitation to classify the martensitic structure as of the Widmanstätten type. Whether the transformation of austenite takes place slowly and completely at a high temperature or rapidly and incompletely at a low temperature, the mechanism of that transformation remains the same. The separating alpha phase is pure alpha ferrite in the one case and alpha iron retaining some carbon in solution, and possibly containing also minute particles of free cementite, in the other.

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[62] E. C. Bain and R. H. Aborn: Nature of the Nickel-chromium Rustless Steel. *Trans.* Amer. Soc. Steel Treat. (1930) **18**, 837.

[63] A. Sauveur and C. H. Chou: Influence of Rate of Cooling on Dendritic Structure and Microstructure of Some Hypoeutectoid Steel. *Trans.* A. I. M. E., Iron and Steel Div. (1930) 100.

V. N. KRIVOBOK, Pittsburgh, Pa. (written discussion).—It seems that in the formation of the Widmanstätten structure the internal stresses should not be overlooked, even though the simplified phase rule (as applied to solids) does not take pressure into consideration. I believe that the formation of the Widmanstätten structure is at times due to the concentrated stresses and that, taking a familiar example, the decomposition of the austenite into martensite is furthered, if not occasioned, by these concentrated stresses. Some experiments to that effect have been carried out recently on austenitic manganese steels, and the results seem to uphold my contention.

Another point may be worth mention. Recently I have participated in work on the iron-manganese system. In these alloys the maximum carbon was found to be in the neighborhood of about 0.01 per cent., while other impurities were practically nil. The modern idea of iron and manganese is that they form a continuous series of solid solutions; yet typical Widmanstätten structures were found in alloys of this type by most of the investigators.

It has been developed recently that the iron-manganese system is probably much like the system iron-nickel. Alloys containing relatively small amounts of manganese are of solid solution type. The limit of solid solubility seems to be very near 1.4 to 1.5 per cent. manganese. On slow cooling of an alloy containing a little less than 1.4 per cent. manganese, a typical solid solution structure was obtained much like that of any pure metal, while on quenching these alloys show typical Widmanstätten figures.

The explanation of the Widmanstätten formation in this case would seem to be that a transformation from gamma into alpha iron could not be suppressed; or rather, the transformation of gamma iron-manganese solid solution into alpha iron-manganese solid solution, and that the formation of the Widmanstätten structure was due, at least to some extent, to the increased pressure along cleavage planes.

We should be exceedingly grateful to the authors for the presentation of the X-ray data. I am certain that this paper will help in understanding results obtained on entirely different systems.

C. S. SMITH, Waterbury, Conn.—This paper seems to me almost epoch-making. After several years, metallurgists undoubtedly will look back to this paper as the beginning of a greatly improved way of studying age-hardening phenomena.

Dr. Sauveur mentioned that slip bands sometimes result in a Widmanstätten structure. I have frequently observed in copper alloys a structure due to slip bands which is very similar to but not actually a true Widmanstätten structure. If an age-hardenable alloy has been quenched at a temperature at which it is homogeneous and then cold-worked, there will be a number of slip bands, or more correctly mechanical twins, which will run across the grains in the various 111 directions. If the alloy is then annealed the planes where slip or twinning occurred, being zones of greatest instability, will be the most prolific source of nuclei, which therefore lie along these planes but do not necessarily bear any relation in orientation to them. This results in a large number of very small plates or needles localized in streaks. Casual observation would then show apparent precipitation along the 111 planes, but studies at a high magnification would reveal the individual particles to be oriented entirely differently. The principle of this can be seen in Figs. 18 and 19. Fig. 18 shows a crystal in which are a few mechanical twin bands. Fig. 19 shows the same crystal after reannealing to cause precipitation, and if it is examined from a distance, so that the individual crystals are invisible, the three directions of the original twin markings alone can be seen. On the other hand, if it is studied more closely the individual crystallites can be seen and their orientations found to be totally different. Such structures are likely to occur in practice, and examples of it can be seen in Figs. 45 to 49

of my paper on the alpha-phase boundary of the copper-silicon-manganese system.[64]

The authors have been endeavoring to determine the orientation of the precipitated phase in relation to that of the parent lattice. It might throw some light on the subject if the orientation of a second phase crystallizing from the liquid state on an already solid primary lattice were studied. A peritectic reaction would provide the best material for this, since comparatively large crystals could be made. In the copper-silicon alloys with less than 7.7 per cent. silicon, alpha first separates, until at 852° C. there is a peritectic reaction which results in the formation of beta. This beta actually coats the alpha crystals and takes an orientation definitely related to it. An unusual reaction in this system results in the formation on further cooling of more alpha. This secondary alpha, taking its orientation from the parent beta, has an orientation which is apparently that of a twin to the primary alpha. The copper-silicon system is also unusual in that there is a loop in the alpha boundary, so that in addition to
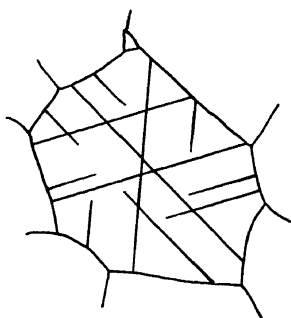
FIG. 18.   FIG. 19.

FIG. 18.—CRYSTAL CONTAINING A FEW MECHANICAL TWIN BANDS.
FIG. 19.—SAME CRYSTAL AFTER REANNEALING TO CAUSE PRECIPITATION.

getting a Widmanstätten structure of gamma in alpha on cooling, one can also obtain a similar structure of beta in alpha on heating into the high-temperature duplex zone.

The importance of the structure of the precipitated phase in determining the manner of precipitation is well brought out in the paper. It would seem from this that when a true compound separates the manner of nucleus formation would be different from when the precipitated phase is a solid solution. It is generally agreed that compounds have a more or less definite arrangement of atoms, the atoms of one metal having a definite position in relation to the atoms of another, while in solid solutions the atoms generally are mutually interchangeable. This would apparently make it considerably more difficult for a suitable arrangement of atoms fortuitously to occur in the form of a compound nucleus.

One system which would be worthy of study is that of copper and silver. At both ends of the diagram there is a change in solubility which would certainly give rise to Widmanstätten structures. This system is unusual in that both the parent lattice and the constituent that is precipitated have the same structure, face-centered cubic, and it is possible to precipitate either constituent from a parent lattice of the other.

(Written discussion).—There is a possible influence of twins in determining the orientation of the nucleus and the direction of growth. Although the authors took care to avoid obviously twinned crystals, it is still possible that the formation of a

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[64] C. S. Smith: Alpha-phase Boundary of the Ternary System Copper-silicon-manganese. *Trans.* A. I. M. E., Inst. Met. Div. (1930) 164.

crystal of precipitate would result in sufficient straining of the lattice to produce a twin in its immediate vicinity. It is even possible that twinning actually precedes growth, and if this is so the 12 directions which the authors have observed in copper-silicon alloys are easily accounted for. The copper-silicon system is particularly susceptible to mechanical twinning, which is apt to develop even during the polishing of specimens for microscopic examination unless great care is used. Twins would almost certainly be produced at least locally by the strain following the formation of a precipitate, even if they were not first produced by quenching strains.

R. S. ARCHER AND L. W. KEMPF, Cleveland, Ohio (written discussion).—We have made some tests on aluminum-silver alloys. Alloys containing 30, 40 and 50 per cent. silver were prepared from electrolytically refined aluminum of about 99.95 per cent. purity. The 30 per cent. silver alloy was rolled into 14-gage sheet, and chill-cast
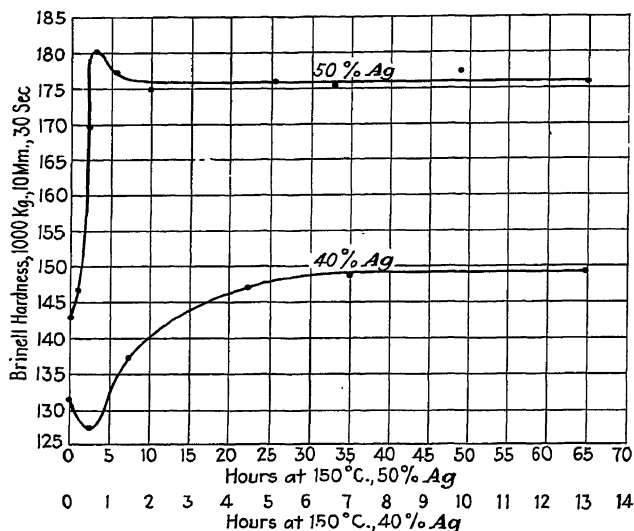
FIG. 20.—PRECIPITATION HARDENING OF ALUMINUM-SILVER ALLOYS AFTER SOLUTION
HEAT TREATMENT AT 530° TO 550° C.

specimens were made of the alloys containing 40 and 50 per cent. silver. The silver contents of the 30 and 50 per cent. silver alloys were 30.56 per cent. and 48.67 per cent. respectively. The 40 per cent. silver alloy was not analyzed.

After heating 25 hr. at 550° C. and quenching in water, the Brinell hardness of the 50 per cent. silver alloy increased from 144 to 148 on aging two weeks at room temperature. No change in hardness during a similar period of room-temperature aging was detected by scleroscope tests on 30 per cent. silver sheet after solution heat treatment.

Fig. 20 shows the effect of reheating at 150° C. on the hardness of the 40 and 50 per cent. silver alloys after solution heat treatment. The solution heat treatments consisted of 24 hr. at 530° C. for the 40 per cent. silver alloy, and 25 hr. at 550° C. for the 50 per cent. silver alloy.

An initial softening is shown in the 40 per cent. silver alloy, as in some other alloys previously investigated. Failure to observe this initial softening in the 50 per cent. silver alloy may be due to insufficiently frequent tests during the early stages of reheating.

Tensile tests were made on test bars of ½-in. dia. of the 50 per cent. silver alloy cast to size in permanent mold with the results shown in Table 6. Results of tests on 14-gage sheet of this alloy are also given in the table. These results furnish a good

TABLE 6.—*Results of Tests on 50 Per Cent. Silver Alloy*

Condition	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness
CAST IN PERMANENT MOLD				
As cast.................................	31,700	47,590	5.5	
4 hr. at 550° C., quenched; 3 hr. at 150° C....	49,050	72,000	1.5	170
14-GAGE SHEET				
As rolled.................................	31,130	35,490	7.3	63
Annealed ½ hr. at 325° C.................	19,500	27,490	20.5	48
Quenched from 2 hr. at 540° C., aged at room temperature...........................	37,250	51,260	12.2	89
Quenched from 2 hr. at 540° C., aged 20 hr. at 150° C.............................	46,000	48,440	2.0	110

illustration of marked precipitation hardening, as shown by increases in Brinell hardness and yield strength, with actual decrease in tensile strength, and show how precipitation-hardening effects might be missed by following only the changes in tensile strength. From the standpoint of the slip interference theory of hardening, perhaps the elastic limit of the material would be the best criterion, since we are interested in determining the point at which plastic deformation or slip first begins.

The exact information provided by Mehl and Barrett regarding the crystallography of precipitation in the aluminum-silver alloys is of the kind needed for a better understanding of the details of precipitation hardening. It was pointed out by one of us, as mentioned in the paper, that precipitation in aluminum-copper alloys appears to take place on the octahedral planes and that the precipitated particles were extended rather than equiaxed. A similar manner of precipitation has been shown for Mg_2Si in aluminum by Dix. The precipitation of both $CuAl_2$ and Mg_2Si is accompanied by marked hardening. The precipitation of silicon in aluminum, on the other hand, produces a relatively slight increase in hardness. Precipitated silicon seen under the microscope appears in the form of rounded particles rather than plates or rods. It is possible that plates are formed at some stage of the precipitation but this has not been observed by the writers. This suggests that the Widmanstätten structure may play an important role in precipitation hardening.

S. L. HOYT, Schenectady, N. Y.—Comparing the width of the platelet with the distance between platelets, the ratio is about 1 to 10. The length of the platelet is possibly 100 times its width. This gives two ratios, 10 to 1 and 100 to 1, and it seems to me that those ratios are so striking, they must be accounted for. It has been shown by Volmer, for instance, that a mercury crystal growing at a low temperature in a stream of mercury vapor will grow in one direction at a velocity many times as fast as can be accounted for by the number of mercury atoms that impinge on the front face.

Volmer assumed that mercury atoms condensed on the sides of the crystal and then slid along to the front, and in that way added to the growth in that direction. Pos-

sibly there is a somewhat similar situation here.   There certainly is directional growth of a pronounced character, the precipitate occurring either as platelets or as needles. An experimental method of attack on this point, I believe, is feasible.   It would consist simply of heating up to a high temperature, cooling to some predetermined temperature, and then studying the growth at that temperature, taking into account, also, the nucleation.   By allowing the precipitate to form at this predetermined temperature, the velocity with which it grows in certain directions could be determined experimentally.

Paralleling this with accurate determinations of diffusion velocities at the same temperatures, in the same system, it should then be possible to set up a picture of the diffusion of the foreign atoms in the parent lattice, assuming simply that the precipitate attracts atoms from the adjacent lattice.   If this picture were established quantitatively, it would be evident whether or not such a mechanism as Volmer develops for mercury crystals would have to be assumed for this process.

Incidentally, if this mechanism actually exists, a good reason is obtained for the orientation of the precipitate and its relation to the parent lattice.

L. W. McKeehan, New Haven, Conn.—This paper is a particularly pleasing example of an experimental contribution well supported by reference to the literature of the subject and with due consideration for theoretical matters.   There are perhaps a few places where slightly greater precision may be attained by unimportant changes. In footnote 37 (p. 86) the value of the reference might be increased by stating just what relative orientations of the face-centered taenite and body-centered kamacite are reported by Young.   In the face-centered structure the composition plane between the phases is of the form $\{111\}$.   If we take the particular plane (111) there will be three planes of the form $\{112\}$; that is, $(11\bar{2})$, $(1\bar{2}1)$, $(\bar{2}11)$.   In the kamacite the plane of composition is of the form $\{110\}$.   If we make it the particular plane (110) there are three important planes perpendicular thereto; namely, $(1\bar{1}2)$, $(\bar{1}12)$ and $(1\bar{1}0)$. What Young says regarding the relative orientation of these two structures is that one of the planes of form $\{112\}$ on one side of the composition plane lies 2° from a plane of the same form on the other side.   All the values given by Young agree with this statement but the number of values cited is hardly enough to make it certain that these are the only positions ever present.

In the note after Table 1, better practice would put the minus signs above the affected digits as in the examples just given herein.

On page 92, line 11, "the normals of two of the planes are parallel" means that the normals to these two planes lie in a single plane perpendicular to the surface of section so that the corresponding points in Fig. 5 are found on one line through the center of the figure.

In line 8 below Table 3, it is stated that all the atoms in the close-packed hexagonal arrangement are equivalent.   This is not strictly true, the atoms in the two sets not being obtainable from each other by translations appropriate to the lattice.   (The close-packed hexagonal arrangement has a simple hexagonal lattice.)

A little lower on the same page, where the hexagonal close packing of atoms in a plane is referred to, it would seem better to call the arrangement a triangular close packing.

On page 99, in the fourth line below the equation, "the angles of these planes from the vertical axis" would be clearer if written "the azimuths from the vertical axis to the normals."   It is this same azimuth that is the angle α in Bozorth's notation as referred to near the top of page 101.   Incidentally, I believe this notation is not originally due to Bozorth, but to Polanyi.

On page 109 it seems to be stated that growth along the plane of precipitation would make further growth in regions adjacent to this plane more probable.   It seems to me

that the exact contrary is true. As in this case it is the low-nickel phase that is precipitating, the formation of this phase will increase the concentration of nickel in adjacent regions and make further precipitation less likely. This, of course, is an additional reason why precipitation extends in the plane first started, thus invading regions not yet much affected, rather than spreading spherically. It makes no difference whether the precipitating phase has higher or lower concentration in the rarer constituent, precipitation in the neighborhood of already formed precipitate will be hindered.

R. F. MEHL.—I would be happier in answering these discussions if I had had an opportunity to look up papers, and to quote data and impressive names in reply, for the purpose "of ritual adornment and terror," to quote Hilaire Belloc. But possibly I should delay this more serious business until later, doing the best I can at this moment.

I appreciate Professor Sauveur's point of view on Widmanstätten figures in quenched iron-carbon alloys. Possibly the reason I care to call them quasi-Widmanstätten figures now is simply that I am afraid to call them anything else. There must be processes operating in the austenite-pearlite reactions in quenched steels which confuse the Widmanstätten mechanism. Such, for instance, is the process of slip (to which Professor Sauveur referred) operating in transitions such as obtain in steels. This may well lead, as Dr. Smith pointed out, to the precipitation along certain slip planes, producing a pseudo-Widmanstätten figure, not illustrating the true Widmanstätten mechanism. I prefer, then, to withhold the term Widmanstätten figure as applied to martensite until it can be shown that there is a definite relationship in orientation between the precipitates, whatever they may be, and the parent solid solution.

Karnop and Sachs have published a preliminary note (*Die Naturwissenschaften*, May, 1930) describing some results upon the orientation of ferrite and the tetragonal lattice in quenched hypereutectoid steels. No details of their results were given, but it does appear that the ferrite and the tetragonal lattice in martensite bear a definite relationship in orientation to the austenite lattice, the (111) plane in the austenite transforming directly to the (110) plane in the ferrite or the tetragonal phase. That such a transformation relationship should exist is not surprising—I remember that Mr. Bain suggested it in one of his papers several years ago. We shall have to await the publication of the complete article before we can study the work from the point of view of the Widmanstätten figure.

It is rather embarrassing that I shall have, in answering some of these questions, to refer to work which we have done since this work has been completed but which has not yet been published. The Widmanstätten figures in steels have received considerable attention (from C. S. Barrett and Dana W. Smith) and will be reported in due time. It is an interesting fact that the crystallographic plane demarked by the martensitic "needles" in hypoeutectoid, eutectoid and hypereutectoid steels is in each case the same plane, the octahedral, (111), in the austenite lattice. The crystallographic plane sought by ferrite in a precipitation during slow cooling from a hypoeutectoid alloy is likewise (111), as Belaiew showed years ago. But the crystallographic plane sought by cementite in a precipitation from a hypereutectoid alloy is definitely *not* octahedral, but some plane or planes of high index. Obviously, the mechanisms of precipitation in hypereutectoid steels upon slow cooling and upon quenching and reheating are entirely different. For this reason—without a full report of the work of Karnop and Sachs—and because the constituents of quenched and reheated steels may not be identified with certainty, I prefer for the present to label the martensitic structure "quasi-Widmanstätten."

I am glad to admit, of course, Professor Sauveur's correction on the effect of the rates of cooling upon the Widmanstätten structure in steels. I merely took the

questioned statement directly from Belaiew, who spent much time in studying this problem.

Dr. Krivobok's points are well taken, and I have partly answered some of them in replying to Professor Sauveur. We shall have occasion to discuss the questions he raises in a publication soon to appear.

Dr. Smith's discussion requires almost no reply, for I am in complete agreement with him at nearly every point. As he suggests, care must be exercised in studying Widmanstätten figures because of the tendency of a precipitate to appear along slip planes, forming a pseudo-Widmanstätten figure, not at all representing the true crystallographic tendency of the precipitation. It is for this reason that certain apparent Widmanstätten figures, like that in martensite, in which the constituents cannot be resolved with certainty, are named quasi-Widmanstätten figures. This term is used simply as a temporary label, to be removed if subsequent analysis should show that the figure is in fact a true Widmanstätten figure the crystallography of which is not confused by secondary effects such as slip, instability at grain boundaries, and the like.

Whether the chemical nature of the precipitate—an intermetallic compound, an intermediate solid solution, or a terminal solid solution—should be reflected in the type of figure obtained is impossible to state at present, though such an effect should certainly be sought in a comprehensive study. Possibly further research will answer this.

We have been planning to do some work on copper-silver alloys. The interest this system arouses is just as Dr. Smith states it: from the standpoint of Widmanstätten figures the two precipitations that may be effected may be considered reciprocal; in one case, a precipitation of the silver-rich solid solution from the copper-rich solid solution and in the other that of a copper-rich solid solution from the silver-rich. If the Widmanstätten figure can be produced in a sufficiently well-defined form the study of these alloys should be fairly easy. There is always the danger in this study that the precipitate, first forming as plates, may coagulate and the resulting structure be too poorly defined for crystallographic analysis. In fact, the most time-consuming part of this work is in the production of a figure suitable for study.

Mr. Archer's discussion is interesting. It seems obvious that any facts discovered about the crystalline habit of a precipitate from a solid solution should be of immediate importance to theories of age-hardening. The age-hardening of aluminum-copper alloys has interested me greatly since Mr. Dix published a photomicrograph of a 1.4 or 1.5 per cent. copper alloy showing a very nicely defined Widmanstätten figure. Dr. Barrett has given some study to this alloy, and though I possibly should not speak too much of unpublished results, I should like to say that our present information suggests that the plane of precipitation in a 1.5 per cent. copper alloy is the (100), though when the alloy contains 4 to 5 per cent. copper another plane is chosen, of much higher index than the cube face, a plane which we have not yet identified. The increasing concentration of copper may alter the crystallographic dimensions of the solid solution to such a degree that another pair of conjugate planes in the two lattices becomes operative, giving a Widmanstätten figure of an entirely different appearance. If this is the case, there should be a transition range in copper concentration where the plane of precipitation changes from one to another. Such a transition in the mechanics of precipitation might well be reflected in a discontinuity in the aging behavior as a function of copper content. It would be interesting to have some data on this point.

The lack of a Widmanstätten characteristic in Al-Si alloys might be ascribed to effects of surface tension in the precipitated particle, but since I have not studied this alloy I cannot say much that is definite. There is one more possibility which I should mention, however. It is possible that the precipitate in this system takes the

form of small polyhedrons, as Mr. Marzke, in our laboratory, has observed in the precipitation of the γ solid solution from the β in the Cu-Zn system. The surface tension effect would not have to be great to render the external form indefinite in outline, resulting in spheroids, as Mr. Archer described the precipitated particles.

The possible relationships of Widmanstätten figures to the age-hardening process are interesting. If the true explanation of the age-hardening process is a blocking of slip planes by precipitated particles, the external form of these particles is of great importance. It is clear that an age-hardening theory should not be built alone upon the assumption of small equiaxed particles critically dispersed but should also specify what effect would be expected when plates, needles or polyhedrons precipitate, and what should be the effect of the choice of different crystallographic planes for the formation of the precipitate.

It should be mentioned in passing that there is now considerable doubt that age-hardening is caused by a blocking of slip planes by precipitated particles. Excellent experimental evidence has been advanced to show that the hardening process takes place *prior* to the appearance of the new phase and is associated with a lattice distortion induced by a metastable state preceding precipitation. Whether there should be any relationship between the crystallography of the precipitation process and the state of strain preceding the precipitation cannot now be said.

We have so far given but little attention to the ideas brought out by Dr. Hoyt, but it is clear that they are pertinent. The present theory to explain these figures is simple: The arrangement of atoms upon a plane in the solid solution lattice is very similar to that upon some plane in the precipitate lattice. When during cooling the temperature of precipitation is reached, nuclei form upon the particular plane in the parent solid solution lattice bearing the conjugate relationship to some particular plane in the precipitate lattice, and the first lattice simply transforms to the second with a minimum shifting of atoms. Since the plane in the first lattice is therefore much favored for precipitation the growth of the particle should take place along this plane very rapidly, but as the plane grows some impoverishment must obtain along this plane, resulting in a hindrance to growth so that growth velocities normal to the plate surface become effective and the plate takes on an appreciable thickness.

Obviously a quantitative treatment of the growth of these figures upon the basis of diffusion velocities would be desirable, but at present so little is known concerning diffusion in solid solutions that there would be great difficulties in such a study.

R. F. MEHL AND C. S. BARRETT (written discussion).—We have not observed the formation of twin bands on the solid solution matrix during precipitation, mentioned by Dr. Smith. It must be admitted that precipitation induces some strain in the lattice owing to volume changes, and that this strain might well alter some of the precipitation characteristics, and should therefore be considered as a factor. Some results on the precipitation of the α phase and of the γ from the β solid solution in the copper-zinc system suggest the presence of such an effect, though no suspicion of twinning seemed justified. Without clear evidence of twinning one can only proceed with an assumption of its absence.

We have not described Young's work in complete detail because it did not seem necessary for the present purpose. The details of his work, however, will be important when our work on iron-carbon alloys is published, and at that time sufficient mention will be made.

The changes in nomenclature Dr. McKeehan suggests are all in keeping with good crystallographic practice, though we do not think that any confusion should arise from our nomenclature. Some of our departures from the nomenclature now current among crystallographers were deliberate, as in avoiding the word "azimuth." We have always sympathized with the crystallographers who prefer the term "close-

packed hexagonal" to the term "close-packed triangular," thinking it more descriptive of the lattice type.

The last paragraph of Dr. McKeehan's discussion is extremely welcome.   The processes which take place during the formation of the original nucleus and the growth of that nucleus to a crystal of appreciable size are obscure and little subject to direct analysis.   Any statement must be in the nature of an inference. We have attempted, on page 109, to explain the growth of the original nucleus to a plate on the basis of the close match in atomic patterns and interatomic distances upon the two planes participating in the precipitation making the extension of the original nucleus along that plane rather than any other easier because of the small shift in atoms necessary for the transformation, and then to explain the fact that the precipitated plates have an appreciable thickness on the basis of an increasing tendency towards growth perpendicular to the plate as a consequence of an impoverishment of one of the precipitating atoms on the atomic plane continued through the crystal.

Dr. McKeehan's suggestion of the influence of concentration changes in the matrix adjacent to the plate face is very valuable.   He uses it to explain the plate form of the precipitate, but not the finite thickness of the plate.   The idea of the influence of concentration gradients which he supplies, however, can be extended to explain both facts.

The first nucleus of the precipitate takes the form of a plate presumably because of the similarities in the atomic pattern and the interatomic distances in the two atom planes participating in the crystallographic transition.   This nucleus can form (in meteorites) only by a diffusion of the Ni atoms away from the plate into the
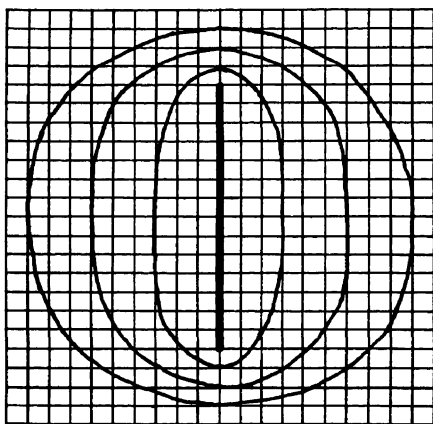
FIG. 21.

FIG. 22.

FIG. 21.—REPRESENTING CONCENTRATION GRADIENTS AROUND A PRECIPITATED PLATE (VIEWED EDGEWISE).

The heavy black line is the precipitated plate in a matrix of the parent solid solution (the network) and the ellipses represent lines of equal concentration.

FIG. 22.—GROWTH OF THE ORIGINAL PLATE NUCLEUS REPRESENTED IN STAGES.

Each successive stage of precipitation deposits more at the plate edge than at the plate surface and the result is a plate lenticular in shape.

adjacent matrix of undecomposed solid solution. The process of diffusion will result in concentration gradients around the plate, which will be steeper at the plate edges than at the plate face. Diagrammatically these concentration gradients may be represented (Fig. 21) by equiconcentration lines.

Further growth of this plate (upon decreasing temperature) can take place only by a further diffusion of Ni atoms away from the plate. At the plate edges, where a steeper concentration gradient obtains than at the plate face, the diffusion of Ni atoms will be most rapid, and the nucleus will tend to increase in size by growth along the plane of the plate rather than perpendicular to it.

Diffusion is not absent, however, perpendicular to the plate face; it is merely less there than at the plate edge, and accordingly there must be some growth by the

FIG. 23.—WIDMANSTÄTTEN FIGURE PRODUCED BY PRECIPITATION OF IRON NITRIDE FROM SOLID SOLUTION OF N IN α FE. $\times$ 500.
Showing the lenticular shape of the precipitated plate. Etched with picric acid in alcohol.

addition of atoms to the plate face. It is simply a matter of difference in the rates of diffusion at the two places; the addition of atoms at the edge is more rapid than at the face and the original plate nucleus grows into a large and (microscopically, usually) visible plate. Furthermore, as the alloy cools concentrations richer in the rejected atom (Ni in the example above) will become unstable and will tend to precipitate because of the diminishing solubility of the Ni-rich phase with decreasing temperature. The region of the matrix contiguous to the plate face, enriched with Ni by the precipitation of the plate, will thus on lowering temperature become ripe for precipitation. It seems, therefore, that two processes contribute to the growth of the plate perpendicular to the plate face, though the second process may not be greatly contributory.

The process of growth might be represented as shown in Fig. 22. The original nucleus is perhaps but one layer of atoms. This layer grows by addition of atoms to the edges but simultaneously also by an addition of atoms to the plate surface. For the reasons stated above, the rate of growth at the edges is greater than at the surface

and accordingly each deposited layer will add to the length of the plate more than to the width.   Continuing such a process should result in a lenticular particle, very thin at the edges and thickest in the middle.

A study of published photomicrographs of Widmanstätten figures and some from our own files confirms this conclusion.   The lenticular character of the Widmanstätten precipitate is especially notable in FeS-CuS alloys;[65] suggestions of it can be found in Fig. 13, and it is especially evident in a photomicrograph prepared in this laboratory of the Widmanstätten figure resulting from the precipitation of the iron nitride from the solid solution of N in α Fe (Fig. 23).

It is important to note that from this point of view, except for the form and orientation of the original nucleus, crystallographic relationships between the two participating lattices are not important.   The form taken by the first nucleus, however, so fixes the conditions of diffusion that the grown—and visible—precipitated particle reflects the true shape of the original nucleus, a plate nucleus forming a visible plate (somewhat lenticular in shape because of the diffusion relationships), and possibly a polyhedral nucleus forming a visible polyhedron and also possibly an acicular nucleus forming a visible needle.

Indeed, the matching of the patterns on the two participating atom planes could not have much if any significance beyond the formation of the first nucleus, for after the length of the plate had grown beyond a relatively few atom diameters the small but measurable difference in lattice spacing would throw the atoms on the two participating planes wholly out of registry.

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[65] G. Sachs: Grundbegriffe der Mechanische Technologie der Metalle, 262, Fig. 212.   Leipzig, 1925.   Akademische verlagsgesellschaft.

Studies upon the Widmanstätten Structure, II.—The β Copper-zinc Alloys and the β Copper-aluminum Alloys*

By Robert F. Mehl,† Washington, D. C. and O. T. Marzke,‡ Cambridge, Mass.

A STUDY of the structures arising from the decomposition of the β solid solutions in the Cu-Zn and the Cu-Al systems is of peculiar interest in the study of the mechanism of precipitation from solid solutions. It is possible in these alloys, by varying the composition within the β field, to precipitate from the same basic lattice phases having different lattice structures. It has been rather generally assumed heretofore that the type of structure originating from the decomposition of a solid solution— the Widmanstätten structure—is determined by the lattice structure of the parent solid solution alone. In the first paper of this series[1] evidence was advanced which threw doubt upon this hypothesis; but definite proof of the correctness or incorrectness of the hypothesis should be forthcoming from a study of these alloys, for if the structures originating, for example, from the precipitation of the α phase from β and of the γ phase from the β in the Cu-Zn system should be shown to be crystallographically different, the hypothesis would necessarily be held as definitely disproved. Furthermore, the newer proposal enunciated in the first paper of this series—that the origin of the Widmanstätten structure lies in a cooperation between the lattice of the parent solid solution and that of the precipitate—which at present seems the only alternative hypothesis, would in such an event be given added weight.

The work here reported shows that the Widmanstätten structures originating in the precipitation of the α phase from the β and in the precipitation of the γ phase from the β in the Cu-Zn system are indeed crystallographically different; and incidentally presents some new descriptive information on the Widmanstätten structure from a more general point of view.

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[1] R. F. Mehl and C. S. Barrett: Studies upon the Widmanstätten Structure, I.—Introduction. The Aluminum-silver System and the Copper-silicon System.

PRECIPITATION OF α PHASE AND γ PHASE FROM β PHASE IN CU-ZN SYSTEM

Precipitation of the α Phase

The "needlelike" nature of the precipitate of the α phase has been remarked by numerous writers, yet little exact information may be obtained from a perusal of the literature upon the true crystallographic nature of the precipitate. Owing to the widespread confusion in the use of the designation "needlelike" previously discussed[2] it is usually difficult to understand the precise meaning attached to this term in descriptions of these alloys. Although it cannot be doubted that the truly acicular character of the "α needle"—for which the present work furnishes proof—has been understood by many workers, it is likewise certain that some have assumed the α precipitate to be in the form of plates, for it is frequently stated that the α phase forms upon the cleavage planes of the β, and, by one writer, that it forms along the Neumann planes.

Publications on this alloy have been numerous. No attempt will be made to give complete references. Furthermore, some of the work reported here is largely repetitious, and no apology need be made, for in a study of this kind in which old facts are regarded from a new point of view, some repetition is not only permissible but necessary. Accordingly some heat treatments have been performed and some structures obtained and described which are not new, but which have been selected to bring out special points relating to the Widmanstätten mechanism.

In order to facilitate the discussion of the work, Fig. 1 is introduced, representing the constitution of the Cu-Zn system in the concentration ranges studied. It has been adapted from the work of Bauer and Hansen.[3]

FIG. 1.—CONSTITUTION OF CU-ZN SYSTEM IN REGION OF α PHASE.

Preparation of the Alloy.—For a study of the precipitation of the α phase, an alloy containing 57.3 weight per cent. copper was chosen. This was made from cartridge brass (analyzing 68.00 per cent. Cu,

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[2] R. F. Mehl and C. S. Barrett: *Loc. cit.*, 5, 6; footnote 39.

[3] O. Bauer and M. Hansen: Der Aufbau der Kupfer-Zenklegierungen. *Ztsch. f. Metallkunde* (1927) **19**, 423–34.

31.98 Zn, 0.02 Fe, with an unweighable trace of Sn and no trace of Pb) to which was added high-purity zinc (analyzing 99.987 per cent. Zn), and the mixture melted (the zinc added after the cartridge brass had melted) in a graphite crucible under a borax flux with induction heating. The melted alloy was chill-cast into a steel mold giving a bar 1 by 1 by 12 in. and subsequently hammer-forged hot into a plate $3/8$ in. thick. This plate was annealed at 800° C. in graphite for 24 hr. and quenched in cold water. The quenched plate was then cut into pieces $1/2$ by $5/8$ by $5/16$ in., which served as samples throughout the work. These pieces showed a very coarse granular structure, with the grains occasionally 1 cm. wide on the polished surface.

This composition, 57.3 weight per cent. copper (represented by the left-hand arrow in Fig. 1), was chosen for study because it gave sufficient α precipitate on cooling for the purposes of this study, but not so much that a confused structure, difficult to study, should result. Other compositions, richer or poorer in zinc, gave essentially the same structures, so that the results obtained from the chosen composition may be taken as representative of the range of composition in which β precipitates α.

Heat Treatment and Microstructure of the Alloy.—Although considerable work had been done on the heat treatment of β brass, it was thought advisable to duplicate the work of others in order more closely to study the effects of various types of heat treatment upon the Widmanstätten form of the precipitate.

Most of the specimens were heated in a vertical tube furnace. In the liquid quenching experiments each specimen was suspended by a wire attached to a cover over the upper end of the tube. An atmosphere of nitrogen was maintained in the furnace, sealed at the bottom by a tube containing the quenching agent, so that the specimen, upon the breaking of the wire, passed directly from the nitrogen atmosphere into the quenching agent. The air quenching treatments were carried out in the usual way and need no description.

Two types of heat treatment were used; namely, a controlled rate of quench and a rapid quench followed by a reheating to moderate temperatures for varying lengths of time. Some experiments were made on cooling the alloy just below the temperature of beginning precipitation and then quenching, but the structures obtained with this type of heat treatment did not differ noticeably from those produced by the simpler heat treatments, and will not be described here.

Some experiments were made in order to study the effect of the quenching temperature upon the structures obtained, but no difference in type of structure could be found in specimens quenched from 700° and 800° respectively (Fig. 1). It was thought desirable to study the effects of gradually differing rates of quench upon the $\alpha + \beta$ structure. To this end a selection was made of several of the quenching agents listed by

FIGS. 2–5.—CAPTIONS ON OPPOSITE PAGE.

French.[4] With the size of specimen used in these experiments, however, no noticeable precipitate could be produced with any liquid quench, the first precipitate appearing upon cooling in an air blast from 700° (Fig. 2). As the rate of cooling became slower more of the precipitate appeared, becoming progressively coarser and more rounded, until upon furnace cooling (in graphite in a nichrome box) a structure was obtained in which the α masses were nearly equiaxed (Fig. 3).

In the reheating of the quenched brasses (following a water quench from 700°) the first α precipitate appeared at about 300° C., exhibiting a very fine structure which coarsened somewhat on long heating at this temperature. At higher temperatures the precipitate was coarser and showed apparently a twinned structure (Fig. 9). This twinning may possibly have originated in the residual strains from the drastic quench. In every case, however, this type of heat treatment did not produce so sharply defined a structure as that produced upon slow cooling. Fig. 4 shows a typical structure, obtained by reheating a quenched specimen to 400° for 18 hours.

It seems clear that the conditions for the crystallization of the new phase from slowly cooled and from quenched and reheated solid solutions must be somewhat like those governing crystallization from the melt, so intensively studied by Tammann.[5] We have in this case precipitation from a supersaturated solid solution with two competing processes governing the formation of the α crystals; namely, the rate of nuclei formation and the rate of crystal growth, both dependent upon the temperature. The rate of nuclei formation in this case reaches a maximum at a rather low temperature, whereas the rate of crystal growth reaches a maximum at a higher temperature. The first nuclei forming on slow cooling therefore have an excellent chance to grow to large crystals, and accordingly slowly cooled alloys show large α crystals. But upon quenching the alloy is brought in an unstable state into the temperature range where the rate of nuclei formation is very high and rate of crystal growth relatively low, with the result that many small crystals are formed. No strict application of Tammann's principles can be made to

[4] H. J. French: A Study of the Quenching of Steels. *Trans.* Amer. Soc. Steel Treat. (1930) **17**, 654.

[5] G. Tammann: The States of Aggregation. Trans. by R. F. Mehl. New York, 1925. D. Van Nostrand.

Fig. 2.—Cu-Zn alloy, 57.3 per cent. Cu, cooled in air blast from 700° C. Etched with $NH_4OH + H_2O_2$. $\times$ 90.
Showing α phase as needles in matrix of β phase.
Fig. 3.—Cu-Zn alloy, 57.3 per cent. Cu. Cooled in furnace from 700° C. Etched with $NH_4OH + H_2O_2$. $\times$ 90.
Fig. 4.—Cu-Zn alloy, 57.3 per cent. Cu, quenched from 700° C. and reheated to 400° for 18 hr. Etched with $NH_4OH + H_2O_2$. $\times$ 800.
Fig. 5.—Cu-Zn alloy, 57.3 per cent. Cu, cooled in air from 700° C. Etched with $NH_4OH + H_2O_2$. $\times$ 150.

such a case as this, it must be pointed out, for there are added factors in the changing stability upon lowering temperature (the slope of the curve bounding the β and the $(\alpha + \beta)$ regions) and in the crystallographic processes leading to the formation of the Widmanstätten figure. Even in this case, however, Tammann's point of view is very convenient in studying the effects of heat treatment.

Outward Form of Precipitate.—A casual inspection of Fig. 2 leads one to suspect that the α phase takes the form of true needles or fingers, the elongated grains in Fig. 2 representing needles intersected by the plane of polish nearly along their longitudinal axes, and the smaller grains, approximately as wide as the elongated grains, representing needles intersected by the plane of polish at an appreciable angle.

There can be no doubt that the orientation of the α grains is related to the orientation of the β matrix from which they formed, for needles far removed from one another within the parent grain are distinctly parallel.

This parallelism is clearly evident in Fig. 5. Furthermore, it will be noted that in Fig. 5 there are two sets of long needles, making an angle of about 8°, one of which is distinctly darkened by the etching agent whereas the other is left undarkened. The meaning of this is clear: The similar degree of darkening of the parallel needles is purely an optical effect coming from etch pits on the surface of the needles, the lattices of which are oriented exactly the same with respect to the surface of polish. In other words, the lattices of all parallel needles bear exactly the same relation in orientation with respect to the lattice of the β matrix in which they occur. Thus both the parallelism of the needles in each family (two such families, well defined in length, may be seen in Fig. 5) and the common orientation possessed by the parallel needles are proof of the Widmanstätten nature of this structure.

In order to get more direct evidence upon the needle form of the α precipitate several specimens of a structure similar to that shown in Fig. 2 were polished on two sides with a sharp edge, and the precipitated α studied on the two sides. Specimens which showed long needles on one side would show no needles whatsoever upon the other side. If the α phase were in the form of plates these naturally would exhibit traces of the plane of the plate upon both polished sides. Furthermore, long needles could be noted approaching the edge but could not be discovered on the other polished side, or would appear there as dots. This behavior is shown in Fig. 6, which is a composite photograph, with the two sides, originally at 90°, there brought into one plane, with the edge bisecting it. These are exactly the characteristics which should be shown by a true needle structure. Occasionally needles could be found on the two sides which upon preliminary examination appeared to start from the same point on the edge, but in every case closer examination revealed that one of the "needles" was in fact composed of a parallel series of dots which

appeared to be the cross-sections of true needles. It seems possible that these series of dots indicate that the needles of a family lie parallel to one another upon some atom plane in the β lattice, but this lattice plane could not be determined. The tendency of the α needles to follow one direction preferentially in the β lattice, apparent on the edge of the piece represented in Fig. 6, is especially pronounced at the grain boundary (Fig. 2) and leads to that familiar structure in these alloys that has sometimes been designated as a "fir-tree structure." Fig. 7 shows this structure unusually well developed.

FIG. 6.—CU-ZN ALLOY, 57.3 PER CENT. CU, COOLED IN VERTICAL TUBE FURNACE IN NITROGEN FROM 700° C. COMPOSITE PHOTOMICROGRAPH OF TWO SIDES. ETCHED WITH $NH_4OH + H_2O_2$. $\times$ 120.

It might be thought that the parallel groups of needles lying nearly in a plane just referred to might represent a stage in the coagulation or spheroidization of a true plate structure, but despite the large number of samples studied, representing nearly every conceivable heat treatment, in no case was it possible to discover a single true plate. The occasional planarity of parallel needles is possibly related to some lattice instability, caused possibly by the volume change during precipitation or possibly by the instability inherent in the grain boundary. It should be emphasized that this planarity is only occasional, needles within the β grain ordinarily occurring as individuals (Fig. 2).

It is clear from what has been said that the α phase is in the form of true needles. These needles, however, are not perfect in form. Their edges are frequently very ragged, and their cross-sectional areas often
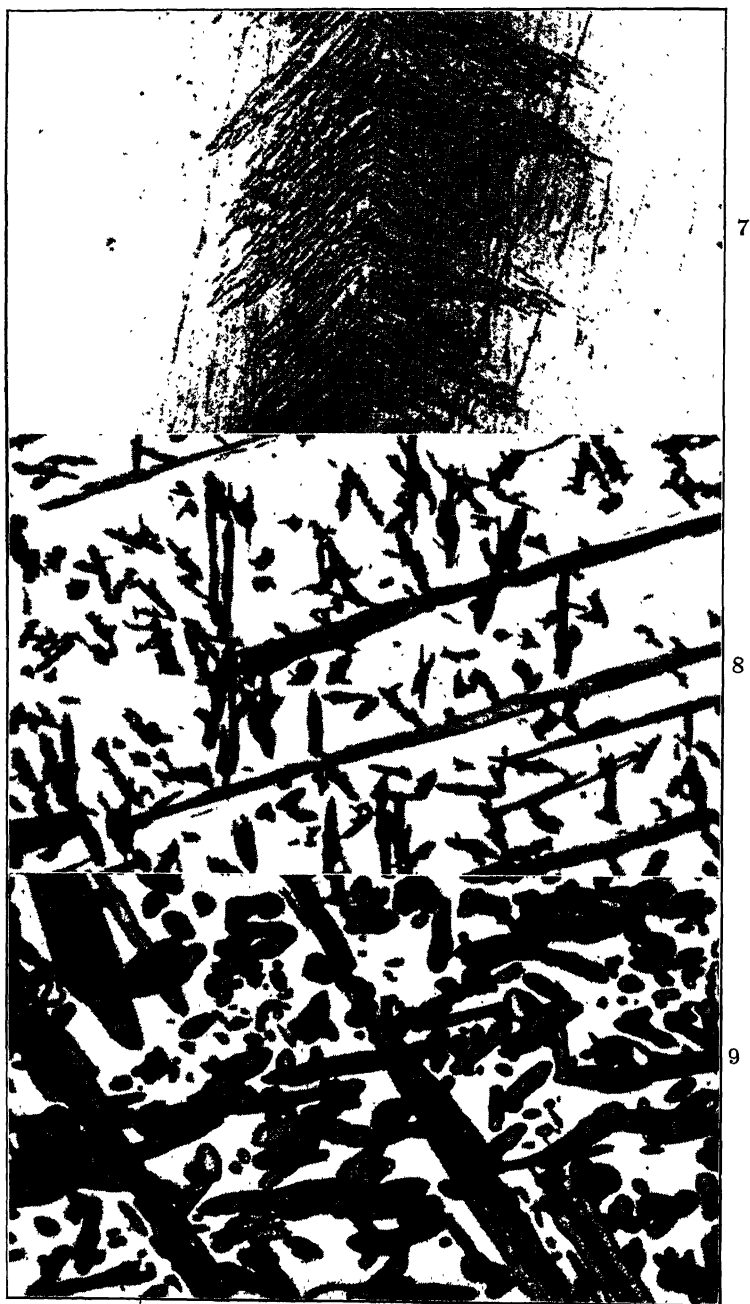
FIGS. 7–9.—CAPTIONS ON OPPOSITE PAGE.

change considerably along the lengths of the needles. There was some suggestion that the needles are more truly lathlike in form than truly acicular, but this could not be confirmed, and the designation "needlelike" seems accurate and sufficient.

The effect of reheating to moderate temperatures upon the structure obtained on slow cooling is of some interest. Fig. 8 represents an alloy cooled in an air-blast from 800° and then reheated to 450° for 3 hr. The form of the long α needles is not changed (Compare Fig. 2) but a rather fine precipitate appeared in the original matrix, indicating that the air-blast cooling was sufficiently rapid to effect some supersaturation in the β phase. The same piece reheated to 525° for 20 hr. showed no change in structure, though reheating at 575° for 20 hr. caused the fine precipitate which appeared upon the first reheating to coalesce into rounded particles of twinned α (Fig. 9).

We have, then, to deal with needles. A complete crystallographic analysis would require that the direction of these needles in the β lattice be determined and that the orientation of the α lattice in the needle with respect to the β lattice in the matrix be also determined. A partial solution is presented for the first of these desiderata; the second presents difficulties which make the determination apparently beyond the resources of present experimentation.

Crystallographic Direction [hkl] of α Needle

For this task several specimens which had been air-cooled from 700° (this treatment gave the best formed needles) were polished on a random cut with the hope that some of the grains might be cut in such a manner that the needles would lie accurately in the plane of polish. The grains which showed the desired structure were photographed after a fine scratch had been put upon their surface for reference purposes. The orientation of the body-centered cubic lattice of the β matrix with respect to the surface of polish and the reference line was then determined by means of the stationary and oscillating film method,[6] the piece so oriented during the exposure that the direction of the reference scratch bore a definite relation to the direction of the X-ray beam and the axis of oscillation. An analysis of the films obtained gave directly the stereographic projection of the β lattice with the reference scratch bearing a

[6] T. A. Wilson: A Study of Crystal Structure and Its Applications, Part XII. *General Elec. Rev.* (1928) **31**, 612.

FIG. 7.—CU-ZN ALLOY, 49.00 PER CENT. CU. ANNEALED 3 HR. AT 800° C. AND QUENCHED IN 5 PER CENT. NaOH SOLUTION IN WATER. ETCHED WITH NH₄OH + H₂O₂. × 540.
FIG. 8.—CU-ZN ALLOY, 57.3 PER CENT. CU, COOLED IN AIR-BLAST FROM 800° C. AND REHEATED TO 450° FOR 3 HR. ETCHED WITH NH₄OH + H₂O₂. × 90.
FIG. 9.—CU-ZN ALLOY, 57.3 PER CENT. CU. COOLED IN AIR FROM 800° C. AND SUCCESSIVELY HEATED TO 450° FOR 3 HR., 525° C. FOR 20 HR. AND 575° FOR 20 HR. ETCHED WITH NH₄OH + H₂O₂. × 90.

definite angular position upon it, which then expressed the orientation of the β lattice with respect to the plane of polish and the reference scratch.

The points on the stereographic projection represent normals to lattice planes and therefore also represent lattice directions.   From the nature
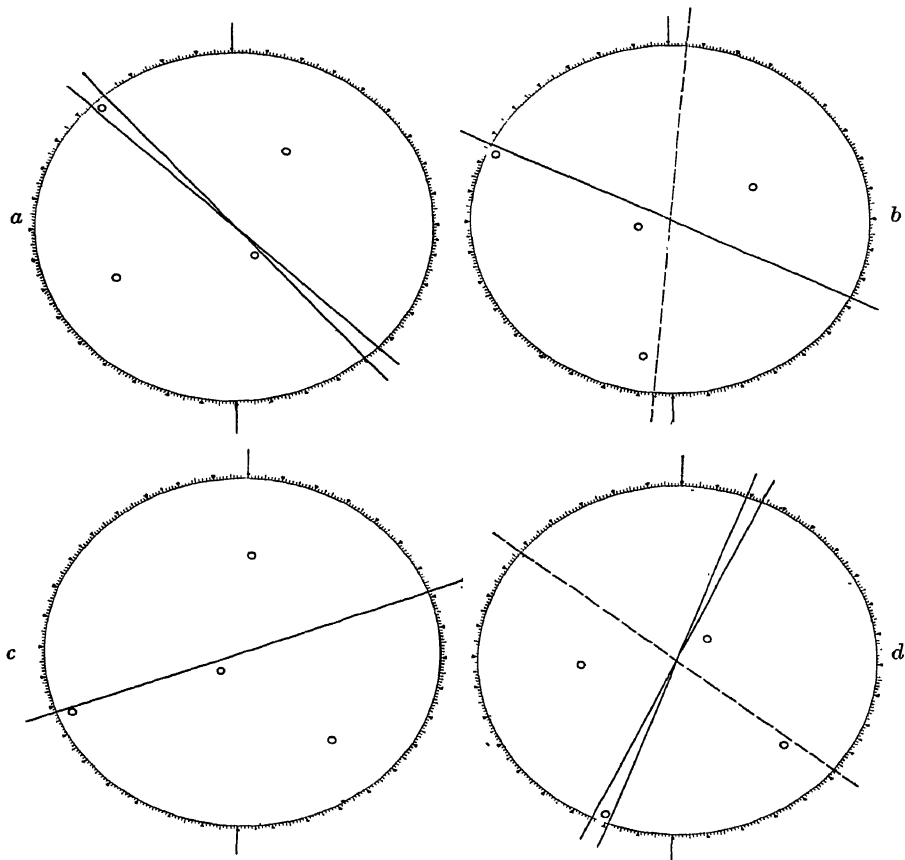
FIG. 10.— STEREOGRAPHIC PROJECTION OF β CRYSTAL.

Small circles represent (111) points and express orientation of β crystal with respect to surface of polish and reference scratch here represented by poles.

Full lines represent directions of long, well-defined needles; dotted lines short needles intersected by the surface of polish at apparently a fairly large angle.   In latter case accompanying (111) point is appropriately well removed from periphery of projection.

of the projection, directions which lie very nearly in the plane of the projection (here the plane of polish) will be represented by points very near to the periphery of the projection circle.   Accordingly the directions of the needles (with reference to the scratch) were plotted upon the stereographic projections of the β matrix, and the projection studied for points near the periphery and coincident with the needle directions.

It was found that all of the needle directions fell near to the [111] direction and showed no tendency to indicate any other direction. Most of the determinations were close enough to [111] to be within the experimental error; several of these projections are given in Fig. 10.

But in addition it was found that in most of the specimens there were two distinct sets of directions making a small angle with each other, both approximating [111]. This indicates that the true direction of the needle is not [111] but some direction near to it, exhibiting several [hkl] values not very different from [111]. Such a direction, as, for example, [556], would show three points clustering about each (111) point upon the stereographic projection.

In an attempt to determine this direction two specimens were cut and polished so that two [332] directions would lie in the plane of polish (the two [332] points lying accurately on the periphery of the stereographic projection). The angle between the directions of the two needles was then compared with calculated value of the angle between two [332]

TABLE 1.—*Measured Angles between Alpha Needles in Beta Brass*

NUMBER OF PAIRS	ANGLE
1	5°
1	6½°
2	8½°
1	8¾°
2	9°
1	11°
1	12½°

directions. The observed angle was 8°, whereas the theoretical is 17°. This indicated a direction of higher index than [332]. Series of measurements were made on several pieces in order to get a more accurate determination of the true angle between the true directions, but these values, listed in Table 1, varied from 5° to 12°, so that no definite conclusions could be drawn.

However, the greatest percentage of the measurements fell between 8° and 9°. Calculations of the angles between any two directions in the same quadrant of various twelve-family directions near to the [111] direction gave the values listed in Table 2. The value 8° to 9° indicated that the true direction in the β matrix along which the α needle falls is very near to [556], which exhibits an angle of 8° 58′ between any two of its members in the same quadrant.

The difficulty in this determination lies partly in the lack of precision in the direction of the α needle, and partly in the lack of precision in the determination of the orientation of the β matrix. Neither the direction of the needle, nor the orientation of the β matrix could be determined to better than 1° (the uncertainty in the direction of the needle was fre-

TABLE 2.—*Angles between Any Two Directions in Same Quadrant of Various* 12-*family Directions Which Lie Near to the* [111] *Direction.*

DIRECTION	ANGLE
112	36° 50'
221	27° 16'
223	19° 46'
332	17° 20'
334	13° 56'
443	12° 40'
445	10° 44'
554	9° 58'
556	8° 58'
665	8° 14'
667	7° 22'
776	7° 16'

quently greater than this), so that obviously it is impossible to select among directions which differ only by fractions of a degree. The best that can be said is that the direction of the needle is near to [556].

Relation in Orientation between α Lattice and ·β Lattice.—That a relationship actually obtains is indicated by the etching characteristics of the needles, as previously stated and as shown in Fig. 5, but no experimental technique is known to the authors by which this relationship could be determined, and at present it must be left undetermined.[7]

Discussion on Precipitation of α Phase

It has previously been suggested[8] that the formation of the Widmanstätten figure lies in the near identity of some crystallographic feature (plane, direction) in the parent lattice and a similar feature of the precipitate lattice. Upon precipitation this feature in the parent lattice transforms to the similar feature in the precipitate with a minimum shift of atoms. Such a point of view proved adequate for the Fe-Ni alloys and Al-Ag alloys discussed in the first paper of the present series. Since the α phase in the alloy now under discussion forms needles instead of plates, the suggestion is strong that there may be a near identity of lattice directions in the two phases and a lack of the near identity of lattice planes which leads to the formation of plates.

The structure and the parameters of the two phases are well known.[9] The α phase is face-centered cubic; at maximum solid solubility (38 per

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[7] It might be pointed out here that a method by which the orientation of a microcrystalline constituent in an alloy could be determined would be of great value, especially in the study of Widmanstätten figures.

[8] R. F. Mehl and C. S. Barrett: *Loc. cit.,* 33–34.

[9] E. A. Owen and G. D. Preston: X-Ray Analysis of Zinc-Copper Alloys. *Proc. Phys. Soc.* (London) (1923) **36**, 49.

A. Westgren and G. Phragmén: X-Ray Analysis of Copper-Zinc, Silver-Zinc and Gold-Zinc Alloys. *Phil. Mag.* (1925) **50**, 311.

cent. Zn) the side of the unit cube is 3.696 Å. The β phase is body-centered cubic and the side of the unit cube for an alloy with 48.5 per cent. Zn is 2.945 Å. In a heterogeneous alloy with 43.7 per cent. Zn, the side of the unit cube for the face-centered phase was found to be 3.695 Å, and for the body-centered cube 2.940 Å. The α solid solution exhibits a random distribution of atoms, but the β solid solution (by

TABLE 3.—*Comparison of Various Planes in Alpha and Beta Brass*

Plane	Atomic Arrangements	Angle between Sides of Figure, Deg.	Length of Sides, Å.
Alpha (f.c.c.)			
(210)	Diamond	48	4.53
(331)	Diamond	26	5.82
(311)	Diamond	33.7	4.53
(511)	Diamond	21.7	6.92
(111)	Diamond	60.0	2.62
(100)	Square	90.0	2.62
(211)	Rectangular	90.0	2.62–6.42
(310)	Rectangular	90.0	3.70–5.85
(110)	Rectangular	90.0	2.62–3.70
(221)	Rectangular	90.0	2.62–7.86
Beta (b.c.c.)			
(110)	Diamond	71.5	2.52
(310)	Diamond	35.0	4.91
(322)	Diamond	26.8	8.90
(141)	Diamond	52.0	4.75
(111)	Diamond	60.0	4.17
(221)	Diamond	36.8	6.59
(100)	Square	90.0	2.945
(210)	Rectangular	90.0	2.945–6.58
(211)	Rectangular	90.0	2.53–4.15
(321)	Not like others		

analogy with the Ag-Zn and Au-Zn systems) is suspected of being regular, with the Cu and Zn atoms arranged upon a CsCl type of lattice; i. e., as if composed of two interpenetrating simple cubic lattices of Cu and Zn respectively.

Table 3 lists the dimensions of the various planes in the two lattices. It is obvious from a study of this table that there is no plane in the α lattice closely similar either in pattern of atoms or parameter to any plane in the β lattice.

Table 4 lists the distances between atoms in the various directions in the two lattices. There are several directions in the α lattice that have almost the same interatomic distances as certain directions in the β lattice.

It is difficult to understand, however, how a near identity of two directions of high index in which the interatomic distances are great (27.25 Å. for [556] in the β lattice) could exercise a determinative influence upon the

TABLE 4.—*Comparison of Distance between Atoms for Various Directions in Alpha and Beta Brass*

Alpha (f.c.c.) $a_0 = 3.695$ Å.		Beta (b.c.c.) $a_0 = 2.940$ Å.	
Direction	Distance, Å.	Direction	Distance, Å.
110	2.62	111	2.55
100	3.70	112	7.21
211	4.53	221	8.82
310	5.85	223	12.13
111	6.405	332	13.79
321	6.92	334	17.35
210	8.28	443	18.85
221	11.10	445	22.25
311	12.27	554	23.85
320	13.34	556	27.25
410 ⎱ 322 ⎰	15.25	665	28.95
		667	32.34
331	16.15	776	34.17
511	19.25		
531	21.93		
533	24.25		
551 ⎱ 711 ⎰	26.42		
553 ⎱ 731 ⎰	28.42		
733	30.6		

form of the precipitate and its orientation with respect to the parent lattice. It seems quite possible that the true explanation of the formation of the Widmanstätten figure in these $\alpha + \beta$ alloys cannot be built upon the simple considerations sufficient for previously studied figures.

If a truly acicular structure is to be explained only by a near identity of crystallographic axes in the two lattices, it would seem permissible to assume that the orientation of the precipitate lattice around this direction could be any whatsoever: the precipitate lattice α could have a rotational degree of freedom, as indicated by the arrow in Fig. 11. Yet the etching characteristics of two nearly parallel sets of needles shown in Fig. 5 and discussed on page 128 demand that the orientations of the α lattice in all parallel needles bear the same relation to the β lattice. Indeed, it seems inevitable that only one orientation of the α lattice with respect to the β could obtain, an orientation in which the β lattice could transform to the α lattice by diffusion and growth with a minimum shifting of atoms. It is possible that the orientation of a precipitated form is influenced not only by the orientation of the first nucleus but also by crystallographic factors governing crystal growth.

At the present time this type of structure is difficult both to study and to explain. A complete elucidation doubtless will have to await the development of more precise experimental technique and of a larger body of experimental knowledge of the crystallography of simpler structures.
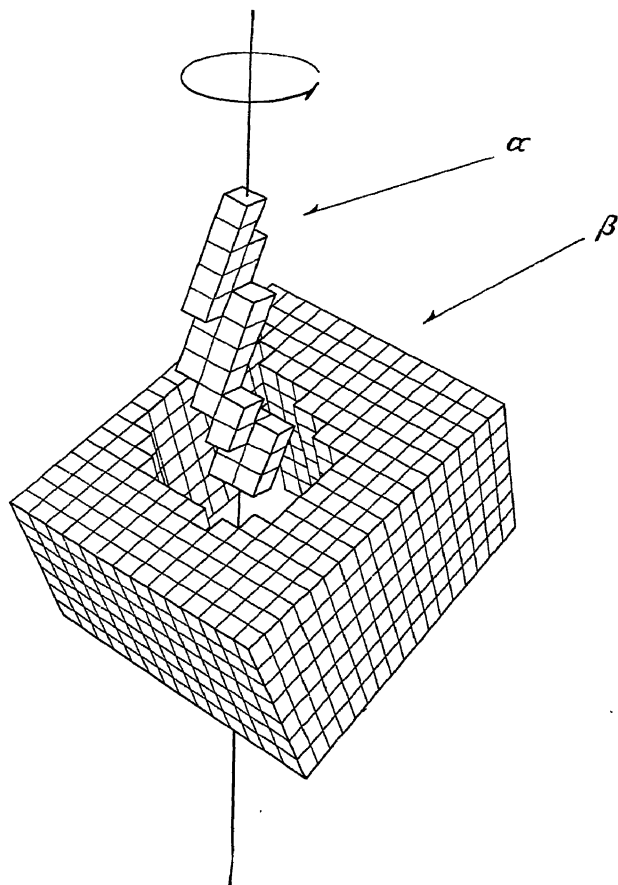
FIG. 11.—DIAGRAMMATIC REPRESENTATION OF α AND β LATTICES IN NEEDLE STRUCTURE.

Precipitation of the γ Phase

Preparation of the Alloy.—An alloy containing 47.8 per cent. Cu (right-hand arrow in Fig. 1) was chosen, and was prepared in the same manner as the alloy used in the study of the α precipitation. The chill-cast alloy was hammer-forged hot from a 1-in. square cross-section to a plate approximately $\frac{3}{8}$ in. thick. This plate was annealed in graphite at 825° C. for 18 hr. and quenched in water. Pieces were then cut from the plate to the dimensions $\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{4}$ in. and served as specimens.

The alloy was extremely brittle and large intercrystalline cracks appeared upon cutting. Many of the specimens could be separated into their individual grains with but little effort.

Heat Treatment and Microstructure of the Alloy. The Outward Form of the Precipitate.—The same general scheme of heat treatment was
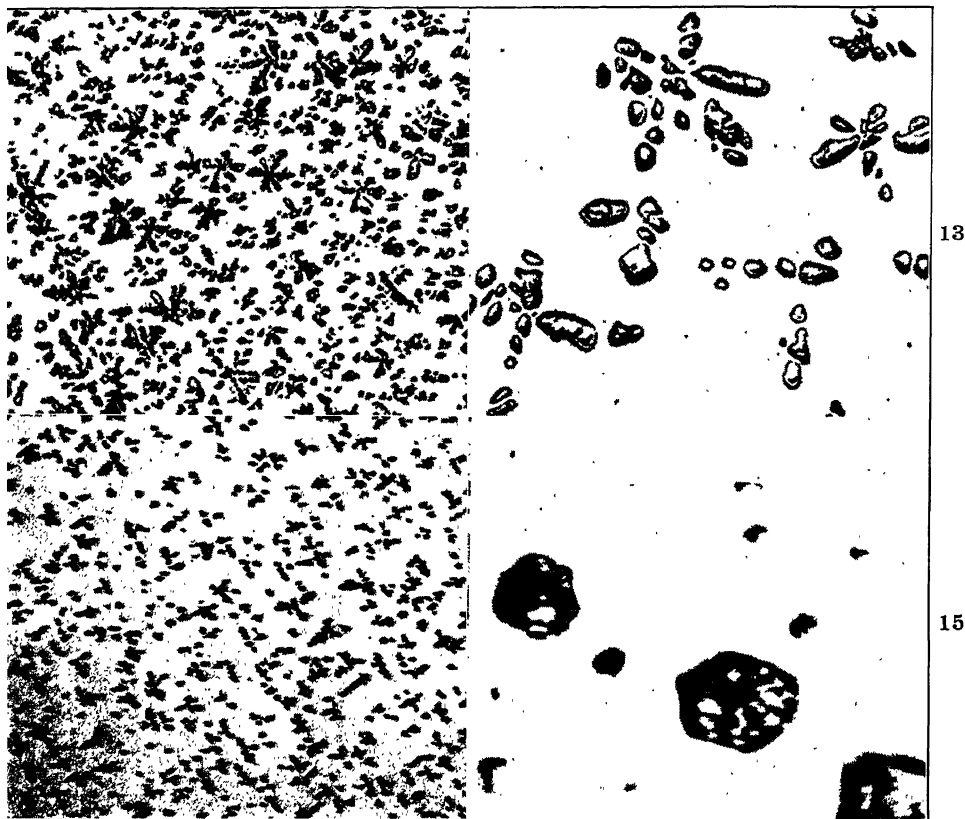
FIG. 12.—CU-ZN ALLOY, 47.8 PER CENT. CU. AIR-COOLED FROM 825° C. ETCHED WITH NH₄OH + H₂O₂. × 150.

FIG. 13.—CU-ZN ALLOY, 47.8 PER CENT. CU. FURNACE-COOLED FROM 825° C. ETCHED WITH NH₄OH + H₂O₂. × 150.

FIG. 14.—CU-ZN ALLOY, 47.8 PER CENT. CU. QUENCHED FROM 825° C. AND REHEATED TO 400° FOR 1 HR. ETCHED WITH NH₄OH + H₂O₂. × 150.

FIG. 15.—CU-ZN ALLOY, 47.8 PER CENT. CU. QUENCHED FROM 825° C. AND REHEATED TO 350° FOR FIVE DAYS. ETCHED WITH NH₄OH + H₂O₂. × 2500.

followed in the study of this alloy as in the study of the alloy that precipitated α. Specimens were cooled from 825° at rates varying from water-quench to furnace-cooling. The first precipitate of any magnitude appeared in the air-cooled specimen. The structure obtained was a distinct "starlike" structure, as shown in Fig. 12. In the furnace-

cooled specimen (Fig. 13) "stars" were also obtained, and appeared to be made up of rather rounded particles of the precipitate; evidently some coagulation had preceded during the cooling of this alloy. The photomicrographs show that the orientation of the separate stars is definitely identical throughout the grain, and since the β lattice is the only common element, it may be said that the orientation of the stars bears a definite relation to the parent lattice, that of the β solid solution; i. e., that the starlike structure is in fact a Widmanstätten figure.

Upon reheating of the quenched specimens the first precipitate appeared after 1 hr. at 400°. The precipitate was again starlike (Fig. 14) but not so completely developed as that obtained on air-cooling. At higher reheating temperatures (1 hr. at 600°) the starlike structure was lost and the precipitate simply had a round appearance.

Especially interesting results were obtained by heating a quenched specimen for 48 hr. at 350°. The gamma phase was found to be in the form of particles having a definite polyhedral shape, with the directions of the edges of the polyhedrons on the surface of polish strictly parallel from particle to particle within a single β grain (Fig. 15). This, therefore, is again a Widmanstätten figure.

This structure is especially suited for crystallographic work, and accordingly several specimens were prepared with identical heat treatment except that the duration of reheating was increased from 48 to 170 hr. in order to increase the size of the particles of the precipitate.

Crystallographic Plane Parallel to Faces of γ Polyhedrons and That Parallel to γ Star "Axes"

The small polyhedral grains of the γ precipitate are most suitable for study. An inspection of the metallographic structure suggested (Fig. 15) that these γ particles are in the form of polyhedrons, each particle similarly oriented with respect to the β matrix. Assuming that the faces of the polyhedrons are parallel to some lattice plane in the β phase, the crystallographic problem becomes simply a determination of that plane.

The crystallographic methods used in the analysis of the α structure are applicable to the present case. Upon the stereographic projection representing the orientation of the β matrix were plotted, not the direction of the sides of the polyhedrons, but perpendiculars to the direction of the sides, since the sides of the polyhedrons are planes, and planes are represented upon the stereographic projection by their normals. In every case it was found that the directions upon the plane of polish of the sides of the polyhedrons could be accounted for by the (110) plane in the β lattice and by no other plane or combinations of planes. Four grains were subjected to stereographic analysis, with the same result. Fig. 16 is the stereographic plot from the grain shown in Fig. 15. This result was

rather expected because it had been observed, previous to the crystallographic analysis, that the number of directions in a single particle was usually 4 or 5, within the maximum number of directions possible for the (110) plane (six) and more than the number corresponding to the (100) plane (three) or the (111) plane (four).[10]

The gamma stars present a more difficult problem. They have the appearance of dendrites (Figs. 12, 13 and 14). Whether they should be regarded as plate structures or needle structures can hardly be determined from an inspection of the photomicrographs. The similarity of
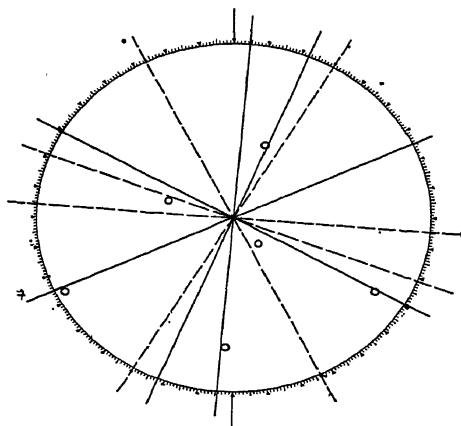
FIG. 16.   FIG. 17.

FIG. 16.—STEREOGRAPHIC PLOT OF TRACES OF SIDES OF GAMMA POLYHEDRONS (DOTTED LINES), THE NORMALS TO THESE (FULL LINES) AND STEREOGRAPHIC POINTS REPRESENTING LATTICE PLANES (SMALL CIRCLES).

Only (110) points are shown. Since lattice planes are represented upon stereographic projection by points coincidence sought is that between (110) points and normals to traces of sides of polyhedrons.
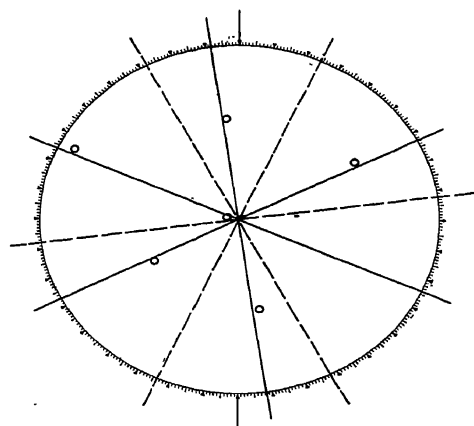
FIG. 17.—STEREOGRAPHIC PLOT OF DIRECTIONS OF "STAR" AXES AND BRANCHES (DOTTED LINES), NORMALS TO THESE (FULL LINES) AND STEREOGRAPHIC POINTS REPRESENTING (110) PLANES (SMALL CIRCLES).

their appearance to that of dendrites, and the crystallographic features of the β lattice they delineate, may offer some hint of their true nature.

Several specimens were photographed and the angular positions of the star axes with respect to a reference scratch determined. These positions were then plotted on a stereographic projection representing the orientation of the β matrix. In each case the directions of the axes accurately coincided with the (110) plane in the β lattice. Three grains, rich in "stars," were analyzed. Fig. 17 is the stereographic plot from one of them.

A close examination of the stars revealed the fact that occasionally the major axes of the stars contained little or no precipitate, the main

body of the γ phase being concentrated in the arms branching from the main axes; usually, however, the main axes were clearly indicated by precipitate. The maximum number of directions observed in the stars was five, as in the case of the γ polyhedrons, and the coincidence with the (110) plane is therefore not surprising.
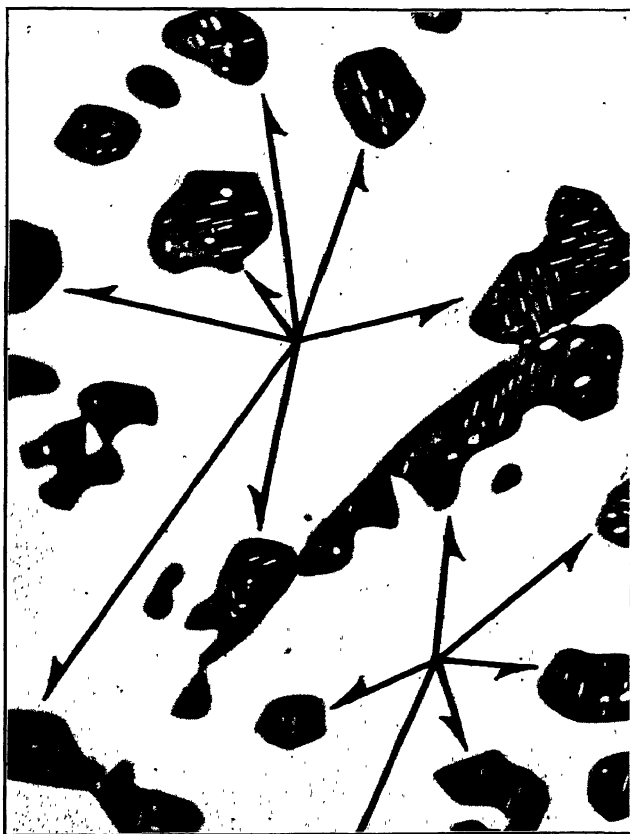
FIG. 18.—CU-ZN ALLOY, 47.8 PER CENT. CU. QUENCHED FROM 825° C. AND REHEATED TO 350° FOR 170 HR., THEN COOLED IN AIR. ETCHED WITH NH₄OH + H₂O₂. × 250.

Arrows indicate precipitate having some orientation as revealed by secondary precipitate.

An interesting series of observations was made upon quenched alloys which had been reheated to 350° C. for 170 hr. and then air-cooled. It was found that within the γ precipitate a precipitation of β had occurred—recognizable by its etching characteristics (Fig. 18). This precipitation can be explained by the slope of the solubility curve delimiting the $(\beta + \gamma)$ and the γ fields (Fig. 1), and since it is quite evident that the

β precipitate itself is in the form of a Widmanstätten figure (Fig. 18) it must be concluded that it formed by the decomposition of the γ solid solution during cooling. The occurrence of this Widmanstätten figure of β in γ must therefore be taken as confirmation for the slope of the solubility curve given by Bauer and Hansen[11] and represented in Fig. 1.[12]

Fig. 18 shows another interesting fact. Three grains are distinguishable. Some of the precipitated γ is intragranular and some intergranular. The γ at the grain boundaries, like the γ within the grain, contains Widmanstätten β, but strangely enough close inspection shows that the striations of β in the γ at the grain boundaries are accurately parallel to the striations of β in the γ within the grains, and the conclusion is immediate that the two types of γ have taken their orientations from the original β and that the γ at the grain boundary is no less Widmanstätten in its nature than the γ within the grain.

This is, so far as the authors are aware, a new fact. It is ordinarily easy to identify the Widmanstätten characteristics of the precipitate within the grain, for it usually has the outward form we designate as the Widmanstätten figure. The outward form of the segregate at the grain boundary, however, is usually indistinct, yet Fig. 18 suggests that it may often bear a definite relation in orientation to the parent solid solution, and may therefore be considered a Widmanstätten figure in the general meaning of the term.[13]

This grain boundary segregate of γ turns a serrated edge towards the β grain to which it bears a Widmanstätten relationship (the arrows in Fig. 18 group the related γ particles) but presents an even edge to the opposite grain. This behavior is clearly evident in Fig. 18 and serves as an additional criterion for the identification of the β grain from which the γ formed by precipitation.

Relation in Orientation between γ Lattice and β Lattice.—No attempt has been made to obtain this information, chiefly because there appear to be no direct experimental methods for the determination of the orientation of microconstituents. Indirect methods—such as that used in the determination of the orientation of the γ phase in the δ in Al-Ag alloys—might be applied, but the near identity in the lattice structures of the β and γ phases would make the determination of the orientation of the γ phase in the presence of an excess of the β phase extremely difficult if not impossible.

The stability of the γ dodecahedrons, however, suggests that the atom planes in the γ phase bounding the dodecahedrons should be planes of

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[11] O. Bauer and M. Hansen: *Loc. cit.*

[12] This example may suffice to indicate the usefulness of the Widmanstätten figure in studies of constitution of alloy systems. Its appearance is proof that a change in solid solubility had taken place during the heat treatment concerned.

[13] R. F. Mehl and C. S. Barrett: *Loc. cit.*, 6–7.

high atomic density. Since the γ phase is body-centered cubic (see below) the (110) plane is the most densely packed, and it is probable that the γ dodecahedrons are enclosed by true dodecahedral, (110), planes. Furthermore, in no Widmanstätten figure yet observed has the external form been so well defined geometrically as that of the γ phase. This may mean that the planes bounding the γ polyhedrons are important planes in the γ phase from the standpoint of crystal habit. If this be admitted, the planes are in all probability the (110) planes in the γ lattice, and the γ lattice forms from the β bodily, the body-centered cubic γ lattice oriented in space exactly as the body-centered cubic β lattice.

However likely such a conclusion may seem, it must be emphasized that the evidence for it is entirely indirect.

Discussion on Precipitation of γ Phase

The structure of the β phase has already been described. The structure of the γ phase is more complicated but nevertheless strikingly similar to that of the β phase. Westgren and Phragmén[14] determined it to be cubic, with 52 atoms to the unit cell, but did not analyze the structure completely. Bradley and Thewlis,[15] working with the photograms obtained by Westgren and Phragmén, accomplished a complete analysis.[16]

The structure of γ brass is cubic. Each unit cell contains 52 atoms, with the side = 8.85 Å. The lattice constant for β brass is 2.945 Å, just one-third that for γ. The γ phase is, like the β, body-centered cubic, and may be considered as built up of 27 unit cells of body-centered β from which two atoms have been eliminated, giving a total of 52 atoms $[(27 \times 2) - 2]$.

This elimination of two atoms changes the positions of the remaining atoms somewhat, but in general the β and γ lattices are almost identical— except for the two vacant lattice points. For this reason it is obvious that there can be no atom plane (or direction) in the β lattice favored above all others for the formation of the γ precipitate, since all planes of the same index in the two lattices are nearly identical and the structure is cubic. If, therefore, the simple ideas thus far presented in this series of papers be even approximately correct it would be expected that the γ lattice should form from the β not in plates or needles but in particles equiaxed in three dimensions, building polyhedrons.

This simple explanation, based upon the three-dimensional similarity of the β and γ lattices, should suffice for the reciprocal case, the precipitation of β from γ illustrated in Fig. 18; that is, an extension of the argument

[14] A. Westgren and G. Phragmén: *Loc. cit.*, 13.

[15] A. J. Bradley and J. Thewlis: The Structure of γ Brass. *Proc.* Roy. Soc. London (1926) **A112**, 678–692.

[16] The analysis of the γ brass structure by Owen and Preston (*Loc. cit.*, 13) may be considered as superseded by the more complete work of Bradley and Thewlis.

to precipitation of β from γ would require that the β phase should form polyhedrons when precipitating from γ. But an inspection of Fig. 18 discloses the fact that the β precipitated in the γ particles is probably in the form of plates. Obviously, then, the simple theory set up is insufficient.[17]

The complexity in the precipitation of γ from β is illustrated by the "stars" obtained upon slow cooling. These have the appearance of dendrites (Figs. 12, 13 and 14), but their orientation in the lattice identifies them as true Widmanstätten figures. The formation of "stars" is not restricted to slowly cooled specimens, but also occurs in quenched and reheated specimens (Fig. 14). The behavior of the precipitated γ appears to be identical in the two cases; the initial precipitate is starlike; slower cooling or reheating to higher temperatures coagulates these stars finally to irregular approximately equiaxed forms (Figs. 13 and 18). With carefully controlled reheating well-formed polyhedrons are developed as an intermediate form in the coagulation process. The loss of distinctness in the polyhedral character of these particles on heating to a higher temperature is simply a surface tension effect frequently observed in other metal crystals.

If we assume that the true crystal habit of the γ segregate is that of dodecahedrons—a solid form bounded by (110) planes—the tendency to segregate initially along (110) plane forming "stars" is difficult to understand. It may be that the formation of "stars" is a secondary effect, conditions by the volume change accompanying the precipitation of γ tending to strain the lattice along the (110) planes, with the result that strained (110) planes radiating from the original nucleus initiate further precipitation of γ by reason of their instability. The formation of "stars" would then be a natural result. In the lack of further evidence, however, nothing definite may be claimed.

PRECIPITATION OF α PHASE FROM β PHASE IN CU-AL SYSTEM

The appearance of the temperature composition diagram for the Cu-Al system in the region of the β field is very similar to that for the Cu-Zn system (Fig. 19). Alloys varying in composition between 91 and 88.2 weight per cent. copper precipitate the α phase upon cooling from the β field. These alloys differ from analogous alloys in the Cu-Zn system in that the β phase is not stable below 535°—the alloys suffer a eutectoid inversion.

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[17] There is one particular in which these two processes—the precipitation of γ from β and the precipitation of β from γ—are fundamentally different; namely, that the formation of γ from β involves the *elimination* of 2 atoms from every 54 atoms of β whereas the formation of β from γ involves the *addition* of 2 atoms to every 52 atoms of the γ. The processes are therefore not truly reciprocal, but it is impossible at present to suggest how this difference should result in a difference in the Widmanstätten figures.

The lattice structures of the β alloys in the two systems are identical in type, and though published data on the structure of the β phase in the Cu-Al system are meager it appears that it is body-centered cubic like the β phase in the Cu-Zn system and that the Cu and Al atoms are not random in their distribution but regular, forming a CsCl structure similar to that formed in the β phase in the Cu-Zn system.[18]

In view of the far-reaching structural analogies in systems of this sort[19] a similarity in structure for the β phases is not surprising.

The close similarity in structure between the phases in the Cu-Al system and the analogous phases in the Cu-Zn systems suggests that a study of the Cu-Al system from the point of view of precipitation structures would be interesting. Alloys richer than the eutectoid alloy precipitate the δ phase or the $\delta + \gamma$ phases, according to the composition, and because of this double precipitation and because it is impossible to develop these structures upon a homogeneous background (the β phase cannot be preserved by quenching) these alloys are less suited for study than analogous alloys in the Cu-Zn system, and have not, therefore, been investigated.

Preparation of the Alloy.—An alloy with 88.9 weight per cent. copper was chosen for study. It was prepared from electrolytic

Fig. 19.—Constitution of Cu-Al system in neighborhood of β phase.

copper cut directly from the cathode and high-purity aluminum (Si, 0.013 per cent.; Fe, 0.012; Cu, 0.021; Al (by difference), 99.954). Correct proportions of the two metals were melted in a graphite crucible with induction

[18] E. Persson: Röntgenanalyse der Heuslerschen Legierungen. *Die Naturwissenschaften* (1928) **16**, 613.

[19] A. F. Westgren and G. Phragmén: X-Ray Studies on Alloys. *Trans.* Faraday Soc. (1929) **25**, 379. A bibliography of publications on structural analogies in alloy systems is included in this general article.

heating under a borax flux, and the melted alloy was cast into an iron mold forming an ingot 1 by 1 by 12 in. This ingot was hammered hot to a 50 per cent. reduction in thickness and annealed 42 hr. at 1000° C. It was quenched in cold water from this temperature and cut into pieces ½ by ½ by ⅜ inch.

Heat Treatment and Microstructure of the Alloy.—It is well known that the β phase cannot be retained by quenching, however, drastic. The structure obtained by quenching is usually described as "acicular β," but an inspection of photomicrographs of quenched alloys (Fig. 20) immediately suggests that the so-called "acicular β" actually represents an early stage in the decomposition of the β solid solution. This structure was observed in the first studies of these alloys, and is now well known.[20]
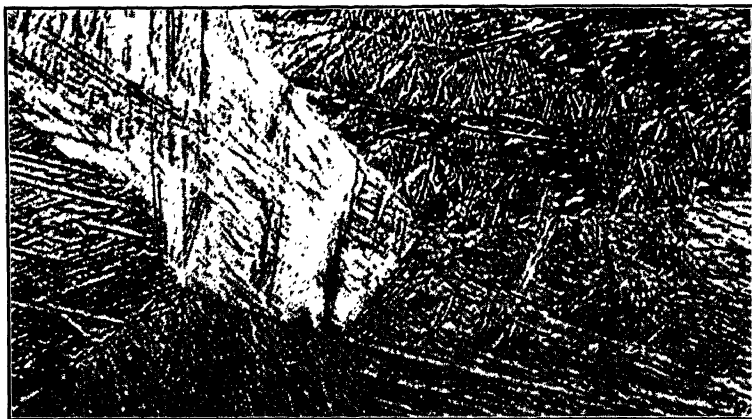
FIG. 20.—Cu-Al alloy, 90.1 per cent. Cu. Quenched from 950° C. in 5 per cent. solution of NaOH in water. Etched in ammonium persulfate. × 80.

The significance of this structure is somewhat uncertain. Attempts to obtain X-ray diffraction photographs from it were unsuccessful, and there can be little doubt that it represents a greatly distorted lattice. It has been suggested that the striations represent twin bands, but a close study of 27 photographs revealed no clear indications of parallel twin bands. Indeed, the twinning of the β phase is characteristically different, for it was observed upon a piece quenched in liquid mercury that, besides the "acicular β," what appeared to be gross twin bands ran

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[20] S. L. Hoyt: On the Copper-rich Kalchoids. *Jnl.* Inst. Metals (1913) **10, 335.**

B. E. Curry: Constitution of Aluminum Bronzes. *Jnl. Phys. Chem.* (1907) **11,** 425.

H. Hanemann and P. D. Merica: Über Kupfer-Aluminum-Legierungen mit 85 bis 90% Kupfer. *Intl. Ztsch. Metal.* (1913) **4, 209.**

across the grains very much greater in width than the striations, and showing the characteristic light and dark etching effects of polysynthetic twinning (Fig. 21). The formation of these twins—if we accept that they are twins—may be ascribed to the shock of the drastic quench.

The designation of the characteristic β structure as acicular is somewhat unfortunate, for the photomicrographs show clearly that the striations must represent the intersection of some lattice plane (not needle) with the plane of polish. It will be shown shortly that in slowly cooled alloys the α phase precipitates as true needles, forming a structure entirely different in appearance from that of the "acicular β." Some traces of this true needle structure may be seen at the grain boundaries in Fig. 20. Largely, however, the structure is "acicular," and it must therefore represent the operation of some process different from that forming the true needle structure. In the true needle structure the metallographic identification of the α phase is unmistakable, and in this case the structure may confidently be designated as a Widmanstätten figure, but the "acicular β" should possibly, at least for the present, be designated as a "quasi-Widmanstätten figure."[21] The high state of strain, which prevents the formation of good diffraction images, and the general appearance of the structure in the photomicrographs suggest that the striations represent the result of a process of slip initiated by quenching strains and by the volume change obtaining from the eutectoid inversion.

Since it was impossible to obtain satisfactory structures by quenching alone, attempts were made to develop the characteristic Widmanstätten figure by varying the rates of cooling from the β field and by reheating the quenched pieces to varying temperatures. One piece, quenched in water from 900° C., gave the characteristic striations, but examination at higher magnifications revealed some incipient precipitation of the α phase (Fig. 22). A specimen cooled in air gave a structure (Fig. 23) strongly reminiscent of the $\alpha + \beta$ structures in the Cu-Zn system, the form of the precipitate suggesting a truly needlelike structure. A furnace-cooled specimen exhibited a structure (Fig. 24) like that of the air-cooled, but the α masses are more rounded, and the eutectoid matrix is better developed.

A specimen quenched from 900° and heated to 400° for $1\frac{1}{4}$ hr. (Fig. 25) exhibited a similar structure, and showed a clearly defined α precipitation initiating at the grain boundary (compare with Figs. 2 and 7). A quenched specimen heated to 575° for 1 hr. gave the structure shown in Fig. 26. The precipitate is now better developed and the general appearance of the structure is strikingly similar to structures developed in Cu-Zn alloys.

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[21] R. F. Mehl and C. S. Barrett: *Loc. cit.*, 8.
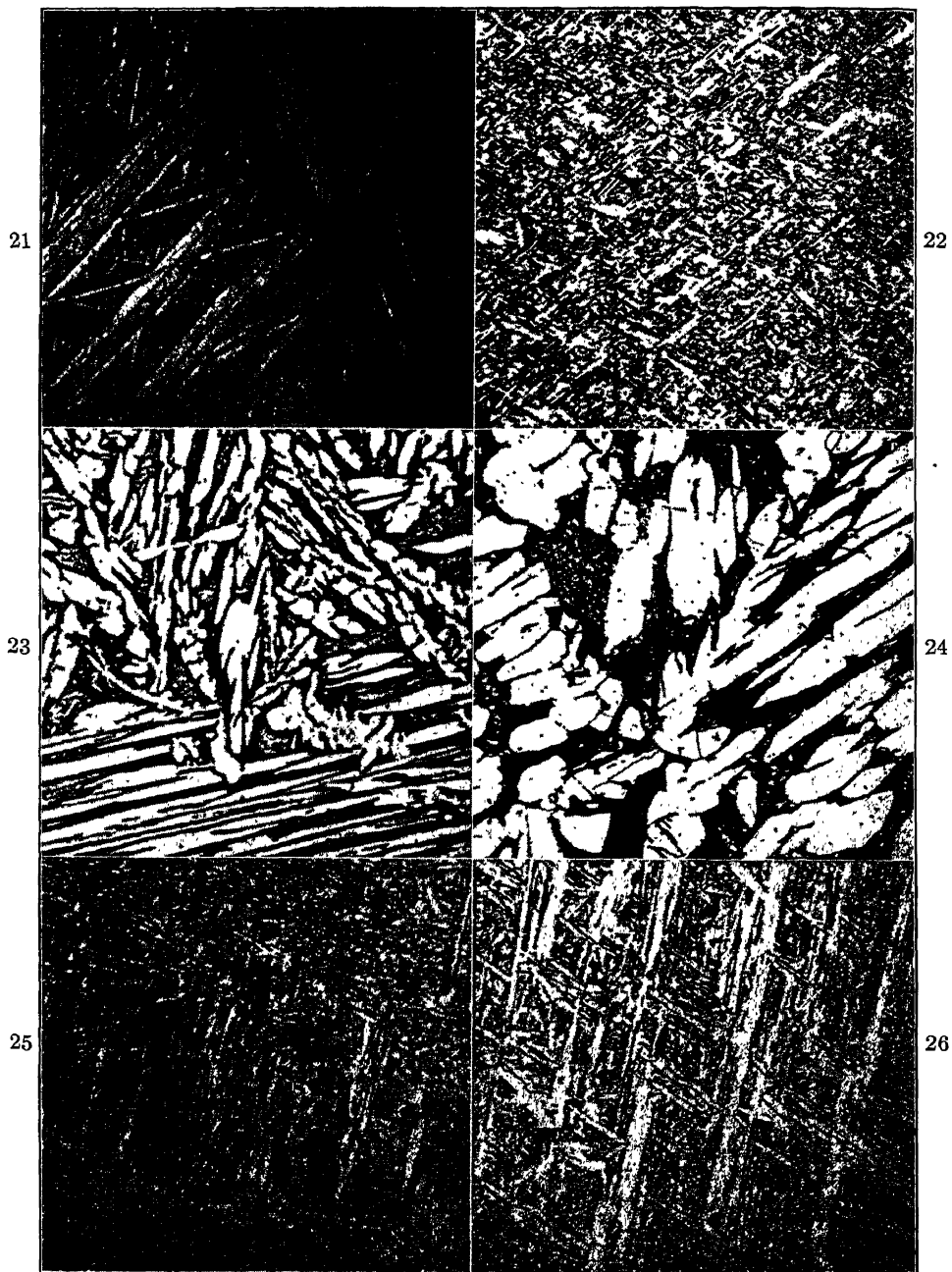
FIGS. 21–26.—CAPTIONS ON OPPOSITE PAGE.

Outward Form of the Precipitate.—Since many of the photomicrographs showed a structure strongly suggesting that the α precipitate was in the form of true needles, an attempt was made to obtain decisive evidence similar to that obtained with the Cu-Zn alloys.

An air-cooled specimen showing a well-defined structure was polished on two sides with an intervening sharp edge (Fig. 27). As in the case of the Cu-Zn alloys (Fig. 6) it was found that long α needles on one side of the edge were not continuous with needles on the other side, but would either disappear on the edge or would appear on the other side as dots. These dots showed some tendency to fall into alignment (Fig. 24) especially at grain boundaries, and, in fact, the same general structural characteristics were observed in this alloy as in the analogous Cu-Zn alloy. The precipitate in this case also, then, is in the form of true needles.

Crystallographic Direction [hkl] of the α Needle

Since the interatomic distances in the β lattice are unknown, no comparison of structural details of the α and β lattices can be made. The impossibility of retaining the β lattice by quenching made it impossible to carry through the type of stereographic analysis used in studying the direction of the α needle in the Cu-Zn alloys.

Indirectly, however, something may be gained by studying the angles between needles on the surface of polish. The angle between the two sets of ong needles in Fig. 26 was measured to be about 62.5°. Specimens frequently were obtained in which two nearly parallel sets of needles could be identified, very similar in appearance to that in Fig. 5. On the relatively few specimens studied, this angle varied between 9.5° and 13.5°. The angle of 62.5° is approximately correct for two [111] directions, but the occurrence of nearly parallel sets of needles indicates, as it did in the case of the Cu-Zn alloys, that the direction of the precipitated needle, though near to [111] is probably a direction of higher index, which, in absence of a precise determination, may be indicated as [hkl] where $h:k:l =$ approx. $1:1:1$.

FIG. 21.—Cu-Al alloy, 86.7 per cent. Cu. Quenched in mercury from 950° C. Etched with ammonium persulphate. × 85.

FIG. 22.—Cu-Al alloy, 88.9 per cent. Cu. Quenched in water from 900° C. Etched with $NH_4OH + H_2O_2$. × 125.
Showing incipient formation of α needles in matrix of "acicular β."

FIG. 23.—Cu-Al alloy, 88.9 per cent. Cu. Cooled in air from 900° C. Etched with $NH_4OH + H_2O_2$. × 125.
Showing coarse well developed β needles in matrix of eutectoid.

FIG. 24.—Cu-Al alloy, 88.9 per cent. Cu. Cooled in furnace from 900° C. Etched with $NH_4OH + H_2O_2$. × 125.
Showing coarse needles of α, somewhat rounded.

FIG. 25.—Cu-Al alloy, 88.9 per cent. Cu. Quenched from 900° C. in water and reheated to 400° for 1¼ hr. Etched with $NH_4OH + H_2O_2$. × 125.

FIG. 26.—Cu-Al alloy, 88.9 per cent. Cu. Quenched in water from 900° C. and reheated to 575° for 1¼ hr. Etched with $NH_4OH + H_2O_2$. × 125.

Discussion of Precipitation of α Phase

It is clear from the foregoing that the precipitation of the α phase from the β in the Cu-Al system is very similar, if not crystallographically identical, to the precipitation of the α phase from the β in the Cu-Zn system. In view of the extensive structural analogies in these systems first demonstrated by Westgren and Phragmén[22] the similarities in the
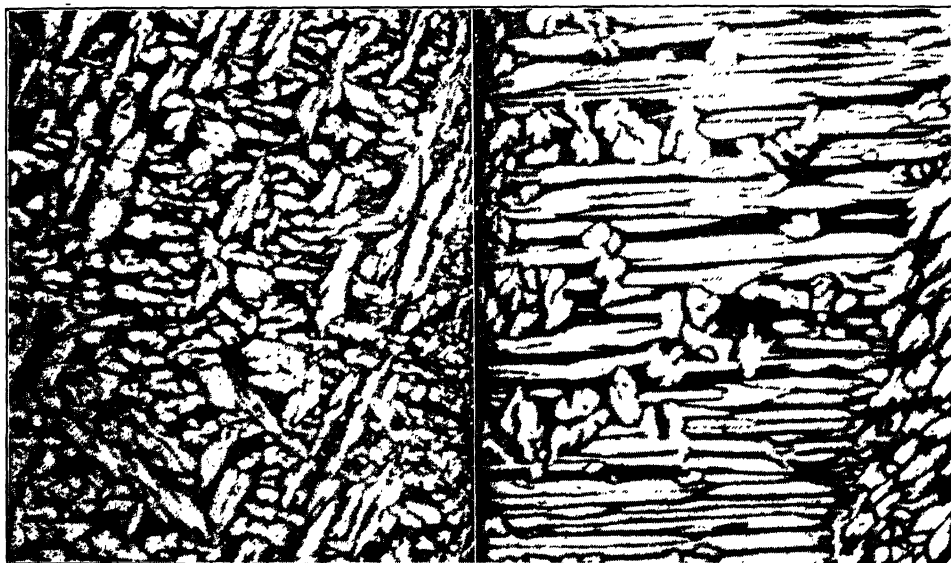
FIG. 27.—CU-AL ALLOY, 88.9 PER CENT. COOLED IN AIR FROM 900° C. COMPOSITE PHOTOMICROGRAPH OF TWO SIDES. ETCHED WITH $NH_4OH + H_2O_2$. × 90.

two precipitation figures are, indeed, not surprising. An extension of the Widmanstätten analogy to other systems showing lattice structure analogies, for example, the Cu-Sn system, might confidently be predicted.

GENERAL DISCUSSION

It is necessary at this time only to point out a few of the major features of this work. From the general point of view the work demonstrates that the Widmanstätten figure may take forms other than that of plates. The α precipitates in both the Cu-Zn and the Cu-Al systems take the form of true needles. The γ precipitate in the Cu-Zn system takes a complicated form, which upon suitable heat treatment resolves itself into remarkably well formed polyhedrons.

The Widmanstätten figure, therefore, may take a greater number of forms than first thought. The only Widmanstätten figures accurately

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[22] A. Westgren and G. Phragmén: *Loc. cit.*

described previously are all plate structures, but it now seems clear that other forms may be assumed.

Crystallographically, the structures described here are difficult to analyze, but a few crystallographic generalizations may be made, nevertheless. It is clear that the crystal structure of the parent solid solution is not the only factor controlling the form of the precipitate, for the forms taken by the α precipitate and the γ precipitate—both precipitating from the same basic lattice type, the body-centered cubic of the β phase—are radically different. It seems necessary to assume that the lattice structure of the precipitate is likewise effective, and that the form taken by the precipitate is a result of a cooperation between the two lattices, and possibly also of the crystal growth behavior in the solid state, about which but little is known.

The data presented may be considered proof that the orientation of the lattice of the precipitated phase always bears a definite relation to the lattice of the parent solid solution. This was found to be true of the kamacite precipitate from Fe-Ni alloys and of the δ precipitate from Al-Ag alloys, and it seems likely that it is a general fact.

This relationship in orientation is probably the basic factor in the formation of Widmanstätten figures. The outward form the precipitate may take, however, is probably also controlled by crystal growth factors, and in the study of Widmanstätten figures both of these factors must be carefully considered. In the lack of extensive experimentation, little in the nature of really comprehensive generalizations can be drawn.

SUMMARY

1. The β copper-zinc alloys precipitating the α phase and those precipitating the γ phase have been studied from the point of view of the Widmanstätten figure.

2. Proof is given that the α precipitate takes the form of true needles, the position and lattice orientation of which are determined by the orientation of the β lattice.

3. The direction in the β lattice taken by the α needles is approximately [111]. Evidence is advanced that three separate families of needles cluster around each [111] direction, which would require a total of 12 families of needles. Measurements of angles between these three families of needles indicate that the true needle direction is approximately [556].

4. The γ precipitate first forms a complex starlike structure. On reheating of quenched specimens the starlike structure divides into a number of minute well formed polyhedrons.

5. The lattice plane in the β phase defined by the intersecting planes forming the stars is the (110) plane, and the plane enclosing the polyhedrons is likewise the (110) plane.

6. The precipitate from the α phase in the Cu-Al system, like that in the Cu-Zn system, is in the form of true needles.

7. The direction in the β lattice taken by these needles appears to be the same as that defined by the α needle in the copper-zinc system.

8. It is pointed out that the present work, taken with previous work, shows that the Widmanstätten figure may be formed of needles, plates or polyhedrons.

9. The Widmanstätten figures obtained lead to the conclusion that the lattice structure of the parent solid solution is not the only controlling factor. It seems certain that in every case the figure forms as a result of an interaction between the lattice of the parent solid solution and that of the precipitate.

10. It is suggested that the structural analogies observed in metal systems may extend to analogies in Widmanstätten figures.

DISCUSSION

(C. H. Mathewson presiding)

A. J. PHILLIPS, Waterbury, Conn. (written discussion).—By the authors' assumption that alpha separates from beta in needles lying along [556] directions or any other set of directions close to the [111], the alpha bands appearing on any polished surface are limited to two groups of not more than three bands each, with a mean interangular distance between groups of approximately 70.5°. For the [556] direction, the least angular distance between directions in different quadrants is 65° and the maximum distance is 80°. However, almost any brass specimen having alpha separated from beta in bands will show a variety of crystals in which the angles between alpha bands will lie outside these limits. Figs. 2 and 4 and the right-hand section of Fig. 6 clearly show bands that from their angular configuration cannot be needles along [556] directions.

In order to check the work of Mehl and Marzke, a piece of ½-in. round rod about 3 in. long containing 62.63 per cent. copper, 0.07 per cent. lead, 0.01 per cent. iron and 37.29 per cent. zinc (by difference) was heated to 875° C. for ¼ hr., furnace-cooled to 775° C. and quenched in brine at −6° C. A specimen was then cut from this piece and polished and etched on two faces at right angles to each other. When this specimen was examined under a binocular microscope bands of alpha in three different crystals could be traced from one polished surface to the other. For convenience in manipulation, a second specimen was prepared with polished surfaces lying at 135° to each other. Both surfaces of this specimen are illustrated in Fig. 28. It should be noticed that there are at least two different crystals in which bands can be clearly traced over the edge from one surface to the other. Fig. 29 shows a composite photomicrograph of a section of the same specimen at a magnification of 75. I believe that the large central band proves that alpha has at least a tendency to separate from beta along crystallographic planes.

In discussing a recent paper,[23] I pointed out that under certain conditions alpha tends to separate along mechanical twin bands in beta. If it is assumed that body-
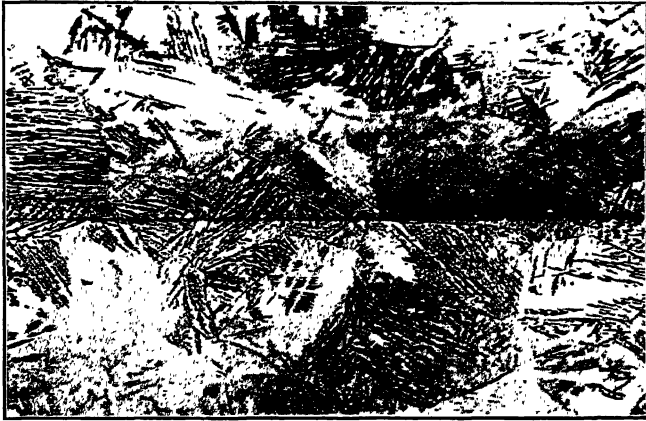
FIG. 28.—CU-ZN ALLOY, 62.63 PER CENT. CU. FURNACE-COOLED FROM 875° TO 775° C. AND QUENCHED. MACROGRAPH OF TWO SIDES. ETCHED WITH NH₄OH + H₂O₂. × 10.

centered-cubic beta brass twins along the same planes as body-centered-cubic iron [the (112)], it would be predicted that at least under special conditions alpha would be

FIG. 29.—SAME MATERIAL AS FIG. 28. COMPOSITE PHOTOMICROGRAPH OF TWO SIDES. × 75.

found lying along (112) planes of the parent beta crystal. To test this the data given in stereographic projection d of Fig. 10 are reproduced in Fig. 30 with the addition

[23] L. R. van Wert: Some Observations in Heat Treatment of Muntz Metal. *Trans.* A. I. M. E., Inst. Met. Div. (1929) 505.

of the poles of the (112) planes and the perpendiculars to the traces that represent the alpha bands. In every case a [112] pole lies very close to each of the three perpendiculars to the traces originally given, proving that all the bands represented in the figure could lie on (112) planes. This may be merely a coincidence but in the light of certain additional conclusions that may be drawn it does not seem to be without significance.

Twinning may take place in the body-centered-cubic lattice along three different (112) planes and result in but a single new orientation. Consequently, twin bands in this lattice are defined by three planes rather than by one and bands separating along three different planes may run together with no boundary or discontinuity at their junction. If alpha separates along such twin bands, this same condition would apply to the alpha bands. In Fig. 31 it is clearly shown that alpha bands separating along two different crystallographic planes have the same orientation, since they run together with no sign of discontinuity at their junction. In Fig. 29 three different sets of bands joined together are shown in the circle. The rather unusual structure shown in

FIG. 30.—SAME AS FIG. 10d WITH ADDITION OF POLES OF (112) PLANES AND PERPENDICULARS TO TRACES REPRESENTING "NEEDLES."
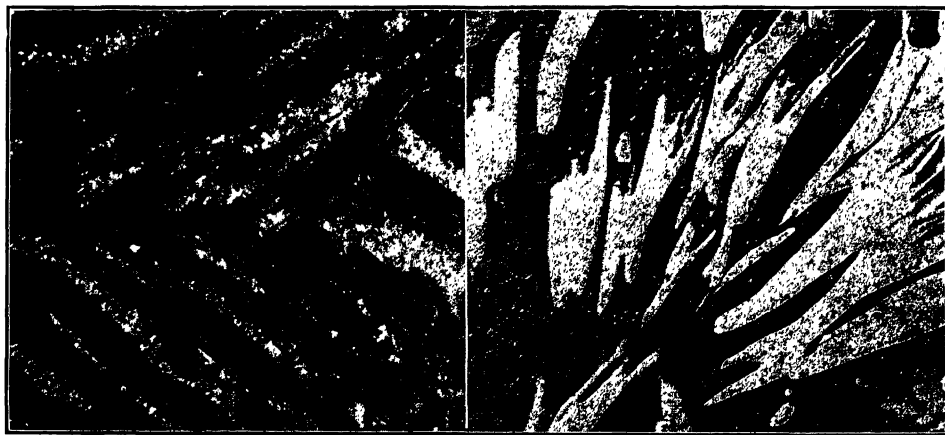
FIG. 31.   FIG. 32.
FIGS. 31 AND 32.—SAME MATERIAL AS FIG. 28. $\times$ 75.

Fig. 32 may be explained by the assumption that the line of intersection of three coordinating planes along which alpha has separated lies at only a slight angle to the plane of the polished surface.

Since separated alpha of a given orientation may be confined by three different planes rather than one, it is not surprising that alpha planes are not always sharply

outlined with straight sides and that some difficulty might be experienced in tracing them from one plane section to another.

C. H. Mathewson, New Haven, Conn. (written discussion).—The simplest way to account for the small angle between the so-called needles represented in the authors' projections, Fig. 10, and the difference of orientation revealed by etching, as in Fig. 5, is to consider that the needles are indeed lathlike (see p. 131) with sides parallel to planes, perhaps of the form {110}, in the zone around the significant direction [111]. This situation is outlined in the projection in Fig. 33.

The plane (111) is shown in the usual manner on a stereographic projection in the (001) plane. The zone in question around [111] is marked by poles of dodecahedral planes (from 1$\bar{1}$0 to $\bar{1}$10) which are assumed to be the planes of precipitation. If the sphere of reference is rotated 35° in the direction indicated by the central arrow around the axis 1$\bar{1}$0–$\bar{1}$10 the pole of (111) comes into the primitive circles at a and the zone referred to above moves into the position of the diameter 1$\bar{1}$0–$\bar{1}$10. This is an ideal orientation for displaying needles crystallizing in the direction [111], which would now lie in the direction of the arrow on this projection. Similarly, the traces of precipitates

Fig. 33.

in any plane of the zone 1$\bar{1}$0–$\bar{1}$10 would also lie in this direction but a slight deviation in orientation, as was evident in all of the authors' projections, whereby the plane (111) changes from a to b would move the zone in question into the position shown by the dotted curve and necessitate a small angle between the traces of any two of its planes in this new plane of projection. Thus a lamella precipitated along the plane 0$\bar{1}$1 would present a trace (needle) in the direction of arrow 1 and one precipitated along $\bar{1}$01, a trace in the direction of arrow 2. These needlelike sections of lamellae precipitated along different planes would, of course, show a difference of orientation on etching. The angle between them would vary with the orientation, and indeed it does not appear that the authors found any strictly definitive angle between their needles.

The authors will object that this interpretation, which of course must have been considered in their analysis of the problem, is not in accord with the experimental observation that needles and not plates are formed. In my own opinion, it is more satisfactory to interpret the microsections of Fig. 6 as representative of precipitation in somewhat raggedly outlined lathlike form on characteristic planes than in needles with significant extension in only one direction. Others have observed a lamellar form in precipitated alpha. Thus, Miss Clark shows[23] that the alpha "reeds" had sufficient depth to stand a large number of polishing operations, including filing and emery treatment.

As to the orientation of the precipitated plates, it is believed that Muntz metal quenched from a high temperature and annealed often shows twinning planes in the precipitated alpha parallel to the plane of precipitation. When high brass is heated into the alpha-beta range and quenched, the shafts of precipitated beta often are formed parallel to twinning planes in the mother crystal. The probable conclusion is that certain hitherto undetermined planes in the beta lattice provisionally assumed to be of the form {110} cooperate with planes of the form {110} in the alpha lattice to initiate the structural transformation in either direction. It would seem quite possible
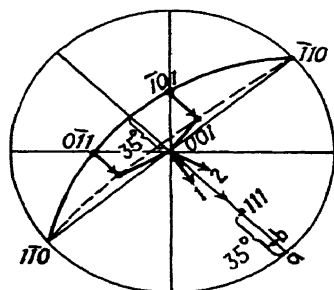
[23] F. H. Clark: Study of the Heat Treatment, Microstructure and Hardness of 60:40 Brass. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 284.

to determine the orientation of the alpha laths or needles shown in the authors' Fig. 5 by straining the preparation and locating two or more planes of slip.   Further-more, the X-ray method used by Mathewson and Edmunds[24] in analyzing the Neumann bands in ferrite might be found applicable.

L. W. McKEEHAN, New Haven, Conn. (written discussion).—The paper is interest-ing in many respects but I will confine my comments strictly to one of the questions it raises.

The authors have presented convincing evidence for a slight divergence of the axis of each α needle in a β-brass matrix from the [111] direction in the parent β crystal. In Table 2 they give the angles between the most nearly parallel directions of the form $[h, h, h \pm 1]$; that is, between [556] and [565].   The angle between $[h, h, h \pm 1]$ and [111] is, of course, less than this.   If h is 4 or more the angle of divergence of the needle axis from [111] is nearly enough $1/\sqrt{3}$ of the tabulated angle; e. g., the angle between [556] and [111] is 5° 03′.   The tabulated angle is that to be expected between two nearly parallel needles if the axes of both lie in the plane of section and if there are three needles in each set.   But if the plane of section contained two needle axes of such a set, the third member of the set would be inclined at only 7° 35′ to the plane of section and if the needles were circular in cross-section the ellipses in which they met the sur-face would be so long in proportion to their breadth (csc 7° 35′ = 7.58) that they would also be listed as needles.   The fact that needle directions occur in pairs rather than in tierces suggests that this pairing is real rather than apparent.   We are therefore led to look for a possible explanation of a rather different kind from that provisionally sug-gested by the authors.

If we examine the table of nearly corresponding distances in Table 4, the first thing we notice is that the distance between atom-centers in the α crystal along a [110] direction is 2.6 per cent. greater than the corresponding distance in the β crystal along a [111] direction.   These are the closest atoms in both gases.   Suppose, then, that a row of atoms along a [111] line in β brass form the nucleus for an α crystal. Such a row in which the Cu and Zn atoms happen to alternate for a short distance would form an ideal foundation.   As the α structure establishes itself and lengthens it finds itself without sufficient headroom.   It is 2.6 per cent. too long to fit in properly. Since the atomic volume is almost exactly the same in the two phases, this may be a potent cause for needlelike growth because the growing needle points are continually pushing their way into the β matrix, reducing its stability, while the needle sides are correspondingly withdrawing from contact with the matrix.

A symmetrical needle of any sort pushing its way exactly along a [111] direction in a perfect face-centered cubic crystal will not deviate from its initial direction, since the pressure distribution it develops is also symmetrical.   But if accidentally deflected at all the pressure on the side toward which it turns will be increased and it may there-fore be expected to grow more rapidly on that side than on the other.   We thus get a rough picture of a mechanism by which a crystal may grow slightly inclined to a [111] direction in the β matrix.   The angle of inclination might be rather variable, and the needle axis would not be a simple crystallographic direction in the α phase any more than in the β phase.   The suggestion that the needles may be lathlike lends some support to this notion, because their axes, on this hypothesis, would be nearly axes of twofold symmetry.   These speculations are probably of interest only in suggesting what the structure of the α needles may be.   We might expect that this divergence would occasionally result in the splitting of a needle, and in Fig. 6 we see at the bottom of the left-hand half such a possible splitting.   Let us hope that somebody some day

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[24] C. H. Mathewson and G. H. Edmunds: The Neumann Bands in Ferrite.   Iron and Steel Technology in 1928, A. I. M. E. (1928) 311.

ιay overcome the very serious difficulties mentioned by the authors as inherent in xing the orientations of the crystal axes in microcrystals which do not scatter X-rays etter than their matrix.

W. P. DAVEY, State College, Pa.—Evidence was given by the writer about five ears ago[25] that crystallization from the melt does not proceed uniformly along a plane urface, but, instead, proceeds along a sort of three-dimensional latticework which is ιter filled in with crystalline material. This means that the material which solidifies ιter in the meshes of the latticework is under tension. Thus all crystals are produced ι a state of strain. If we may transfer this picture to the recrystallization of solids, it ɔllows at once that the direction of the crystals of a new phase must be related to the irection of the original parent crystals. Dr. Mehl and his associates have demontrated that this is indeed a fact, thus lending additional credence to the picture of ow crystals grow. We may therefore bring up, with considerable assurance, some ιteresting speculations on the structure of crystalline materials. For the sake of larity of presentation these speculations will be expressed in terms of crystallization rom the melt. The changes necessary to make them apply to the case of recrystallizaion will be obvious.

If our picture of the mechanism of crystal growth is correct, we must assume that he process of filling in the interstices of the original latticework is identical with the ɩrocess by which this original latticework is formed. That is, needlelike fingers must ɩroject themselves from the original crystal skeleton, and these must send out still ther fingers from their sides so that we may imagine in each pocket of molten material a eplica, on a very small scale, of the original crystal skeleton. The tension of the liquid rom which the new, tiny, three-dimensional latticework is grown may cause slight hanges in crystal orientation, and would certainly produce here and there interplanar pacings which are a little larger than those characteristic of the crystal. These ɩbnormally large spacings might easily be identified with the "pi-planes" postulated by ʼwicky.[26] According to Zwicky, the hypothesis of pi-planes makes it possible to ɩalculate the mechanical properties of metals from their crystal lattices and from the ɩarameters of the pi-planes. The pi-planes become then, a sort of ultra-Widmanstäten structure.

If we imagine the same process of crystal growth repeated in the liquid left in the nterstices of the tiny latticework postulated in the preceding paragraph, we have the .heoretical foundation for the mosaic structure of crystals as revealed by the secondary ɩxtinction effects found in the X-ray examination of crystals. The ordinary picture ɔf the mosaic structure of crystals is, then, related to a sort of ultra-ultra-Widmanstäten structure, and the similar orientation of the various units of the mosaic follows ιs a consequence of the same causes which lie behind the similarity of orientation found ɔy Dr. Mehl and his coworkers for crystals precipitated out from an original ɔarent crystal.

R. F. MEHL AND O. T. MARZKE (written discussion).—Crystallographically the nost fundamental problem to be solved in the study of the Widmanstätten figure is .he problem of the relationship in orientation between the lattice of the precipitate ιnd that of the solid solution matrix from which the precipitate forms. A large body ɔf data of this kind for many different alloys should be sufficient to draw conclusions ɔoncerning the general type of atomic mechanism which leads to the formation of the ïrst nucleus from which the figure forms by crystal growth.

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[25] W. P. Davey: A Theory of the Mechanism of Crystal Growth. Abs., *Phys. Rev.* (1927) **29**, 206.

[26] F. Zwicky: Energy Changes Related to the Secondary Structure of Crystals. Abs., *Phys. Rev.* (1930) **36**, 378.

In general, the outward form of the precipitate offers valuable hints towards a solution of the crystallographic problem. Thus the observation that the kamacite precipitating from taenite is in plates upon the octahedral plane leads directly through orientation determinations to a complete solution of the problem in a manner much simpler than any possible without the observations of the outward form of the precipitate.

The outward form of the precipitate is, however, a problem well worth study in itself. This outward form doubtless is controlled by other processes than the atomic process which leads to the formation of the first nucleus, such as velocities of diffusion, velocities of crystal growth of the precipitate upon different crystallographic planes and direction, internal strains occasioned by the volume changes on precipitation, interfacial energies, and so on—in each case processes which control the growth of the precipitate after the first nucleus has formed.

The outward forms of the α precipitate from the β phase in the Cu-Zn system are much more complicated than those observed in other systems, and, as may be seen from the paper, much less helpful in the crystallographic analysis. Because of this complexity there is not much that can be definitely said—nor has much been said—regarding both the true outward form and the orientation relationships.

At the beginning of the present work it had been hoped that close inspection of the α precipitate would prove it to be in the form of true plates, for these are far more readily studied than other forms. Yet many months' close inspection of many samples of the composition studied gave no certain indication of a plate form. With the evidence available it seemed necessary to conclude that in our samples the α phase took the form of true needles.

We have never seen (an answer to Dr. Phillips' first paragraph) any certain indication of α needles at angles greater than 70°. The needles to which Dr. Phillips refers in Figs. 2, 4 and 6, which seem to exhibit an enclosed angle greater than 70°, are in every case poorly formed needles with indistinct directions. Because of the tendency of needles to lie so close to one another as frequently to seem to merge, and apparently parallel (left center of Fig. 6), and because of the ragged outline of the needles, a random surface of polish will often intersect a needle at a large angle, let us say 30°, and the trace of this needle on the surface of polish will be ragged, uncertain, and often quite deceptive so far as the true direction of the needle is concerned. Because of this uncertainty it is better to measure only the needles that obviously lie nearly in the surface of polish, long needles of unmistakable direction. This has been done in the present work, with no evidence of angle greater than 70°.

Dr. Phillips' pictures are interesting. He should, we believe, take great care in concluding from his Figs. 28 and 29 that α crystals in the form of plates may there be clearly "traced from one polished surface to another." The clearest example of such a crystal given by Dr. Phillips is the large α crystal very near the center of Fig. 29. This crystal, however, has a sinuous (in some cases, we have observed a serrated) outline on both sides of the edge, and remembering that Dr. Phillips' sample contained more copper and therefore gave a bulkier precipitate, it seems highly likely that this apparent continuity represents the very close proximity of two or more parallel needles, all intersected by the plane of polish at such an angle as to render their section roughly elliptical. Such near merging of elliptical sections was observed in many samples and may be seen—not very distinctly—in Fig. 6, especially at the lower left.

It must be emphasized that the tendency to form a truly acicular structure is characteristic of the composition studied in the present work. Such a statement, however, is too attenuated to describe the complexity of the phenomena involved. Probably greater emphasis should be laid upon the tendency of the α needles to lie parallel roughly (at least) upon a plane, as shown in Fig. 6 and discussed upon page 129.

In certain specimens this tendency is very pronounced, so much so that the parallel needles seem in many places to merge and to form a plate[27] (Fig. 34).
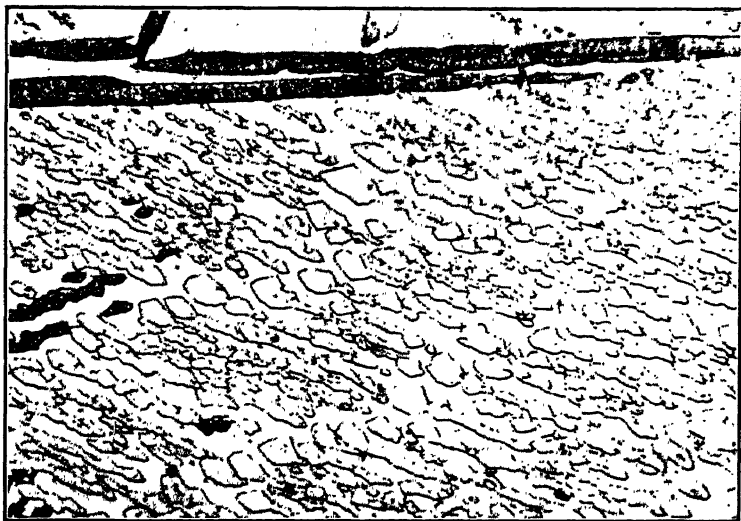
FIG. 34.—CU-ZN ALLOY, 57.3 PER CENT. CU. COOLED IN AIR FROM 800° C. ETCHED WITH $NH_4OH + H_2O_2$. × 250.

FIG. 35.—CU-ZN ALLOY, 57.3 PER CENT. CU, COOLED IN AIR FROM 800° C. COMPOSITE PHOTOGRAPH OF TWO SIDES AT 90°, WITH EDGE BISECTING PHOTOGRAPH HORIZONTALLY. ETCHED WITH $NH_4OH + H_2O_2$. × 100.

[27] It is an interesting fact that many of the needle cross-sections in Fig. 34 show straight sides with a tendency towards parallelism from crystal to crystal.

Their outline remains jagged, however, and quite different in appearance from true plate structures.   If the original outward form of the precipitate is truly platelike, the observed structures can be explained only by assuming the state of granulation to be far advanced.   This tendency towards parallelism should be studied much more extensively, for probably the key to the present mystery lies therein.

The structure shown in Fig. 34 is that shown by the α precipitate when the plane of polish is nearly perpendicular to the needle direction.   It is a structure occasionally found, but the usual structure is one in which the contiguous needles do not come so close to merging.   In the section perpendicular to the plane of polish in Fig. 34 the α precipitate shows a long acicular structure.   This feature of the α precipitate is more clearly shown on Fig. 35 at the left; in the upper left the α is decidedly acicular, in the lower left the α resembles that shown in Fig. 34.

The authors do not wish to go on record with the statement that parallel needles may not in fact merge, especially when the bulk of the precipitate is great and the needles very close and often in contact.   Indeed, the etching effects shown in Figs. 3 and 5 and discussed on page 128 indicate a similar orientation for parallel needles, which would permit the merging of such needles when in contact without a grain boundary in evidence.   Some incomplete studies on slip lines in these α needles show a similar orientation.   The problem of the outward form of the precipitate might be stated in this way: Should the structures observed be considered as truly acicular, constituted of needles which when touching tend to merge into plates with corrugated surfaces, or should these structures be considered as plates which tend to coagulate into needles? Either point of view might be taken from the observations available; we are inclined towards the first.

Dr. Phillips' third paragraph suggests that the α precipitate in the form of plates may be parallel to the most likely plane of twinning, (112).   Neglecting the evidence presented that the α is actually in the form of needles, we believe that the stereographic projections in Fig. 10 preclude such an assumption as that the number of "traces" (needles) lying in the surface of polish (Fig. 10d) is insufficient to account for the number of (112) planes to be expected.   Such a plane would give a maximum of 12 directions, and certainly more than three such directions should be found.   It has been our experience that every grain exhibited the maximum number of such planes. No case of such extensive degeneracy in the number of traces has as yet been observed, nor should such an extensive degeneracy be expected with the study of a large number of grains.

The evidence for a needle lying close to [111] seems good.   Whenever a needle was found to lie very nearly upon the surface of polish (as judged by a uniform width throughout its length) it was found that a (111) point lay very close to the periphery of the stereographic circle and very nearly upon the needle direction.   On the other hand, when the needle was intersected by the plane of polish at an appreciable angle a (111) point lay some distance from the periphery of the circle and nearly upon the needle direction.

The merging of separate α crystals lying upon different planes or along different directions, to which Dr. Phillips refers in his fourth paragraph, may, for all we know, be a true effect as stated above.   It would indicate that the lattices of α crystals with different positions in the α lattice can be coherent; that is, can merge without grain boundaries and form a continuous lattice.   Whether such a condition results from some twinning relationship cannot now be said.

As Professor Mathewson notes, we had some indication that the α precipitate took the form of laths rather than true needles, but the majority of our observations did not seem to support such a conclusion.   Some suggestion of a lathlike structure may indeed be found in Fig. 6, but this is uncertain and usually the directions of the laths on the intersected needle section is very irregular whereas if representative of a true plane, (110), these should show marked directional tendencies.

In fact, the formation of a lathlike structure seems as difficult to understand as that of a needle structure. In all previously examined examples a precipitation along a plane resulted in a plate of nearly equal extension in all directions. This naturally, however, cannot be quoted as evidence against such a structure.

If subsequent research should show that the lathlike structure is indeed the true structure, Professor Mathewson's stereographic analysis explaining the observed etching effects and the observed spreading of needles should be directly applicable. The experimental difficulties in a study of the true outward form of these elongated α crystals are very considerable and a demonstration that the typical structure is in fact a lathlike structure would be by no means easy.

Professor McKeehan's explanation of the small angle found between needles lying near to the [111] direction is ingenious. The difficulty we have had up to the present in attempting to find the third direction postulated by the assumption of [556] does without doubt constitute a weakness in the assumption of [556] as the direction of precipitation. Except for the fact that the angles measured between the needles seemed nearer to that to be expected from two [556] directions than any other there is little reason to have confidence in the assumption of [556]. Two objections, however, can be raised to Professor McKeehan's explanation: (1) The variation in the angle included between two parallel needles (as in Fig. 5) shown by Table 1 represents variations found not upon one piece but from piece to piece. If the scattering in these angular values was caused by accidental deflections of the needle direction during its growth it would hardly be expected that this angle would maintain a constant value over the whole extent of a polished surface of a single grain; (2) two sets of parallel needles (as shown in Fig. 5) show different etching effects, indicating, as stated on page 128, that the needles of one family all possess a characteristic orientation which differs from that of the other family. If, however, the angular divergence between these two sets of needles represents the result merely of a deflection during growth, both families of needles should be different in no way (except direction) and should show similar orientations. It strikes us that Professor Mathewson's explanation of this phenomenon is the most attractive yet suggested.

Professor Davey's discussion is especially welcome, for it touches upon one of the most difficult phases in attempting to rationalize Widmanstätten structures; namely, an evaluation of the effect of strain resulting from volume change upon the type of structure formed. This was discussed briefly in the first paper of this series[28] and in its discussion; but little is known accurately about it. In a complete elucidation of the factors controlling the formation of the structure it will have to be considered, especially with those structures formed on the reheating of quenched alloys, structures of the martensite type like that shown in Fig. 20. It does not seem likely, however, that Zwicky's "pi-planes" should be directly related to the planes upon which precipitation occurs. Such a suggestion was made to us some time ago by Professor Polanyi, and the objection was advanced that the plane of precipitation of the iron nitride from the solid solution of N in α Fe (to be reported upon fully later) is (210) in the Fe lattice, a plane so unusual as to seem quite unlikely as a plane of cleavage or as the plane that defines a crystalline mosaic, the "pi-plane."

The work which we have reported in this paper is being continued and shortly should result in more definite answers to some of the moot points.

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[28] See page 78

Application of X-rays in the Manufacture of Telephone Apparatus

By M. Baeyertz,* Chicago, Ill.

Since 1915 many papers and books have covered industrial applications of X-rays from various angles. Two of the more recent are a paper by Fink and Archer[1], which describes in detail the technique of radiography, and a paper by Clark[2], which embraces the whole field of X-ray metallography. This paper, therefore, is confined to work of the X-ray Laboratory of the Western Electric Co., which naturally divides into two categories: radiography and diffraction patterns of various types.

Radiography

Radiography is the field in which the application of X-rays has had most general appeal among the industries which produce or use metals and alloys. Equipment permitting the examination of heavy sections of metals less permeable than aluminum or other light alloys requires apparatus capable of generating hard X-rays over a considerable period of time. The equipment used in the work presented in this paper is practically identical with that described by Fink and Archer in their paper on radiography in industry and is easily capable of penetrating $\frac{1}{8}$ in. of lead.

Radiography is used in two major groups of problems: (1) in the development of equipment and tools and (2) in studies of materials. So far there has been no instance in which the use of radiography for routine inspection is justified. This is partly due to the fact that the manufacture of telephone apparatus involves the production of many identical parts by standardized procedures and equipment that has had development and trial before being put on a regular production basis. It is during this stage of development of equipment and tools that radiography has been used to particular advantage.

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* Metallurgical Development Dept., Western Electric Co.

[1] W. L. Fink and R. S. Archer: Radiography as a Tool in the Metal Industry. Amer. Soc. Steel Treat. (1929) 16, 551–590.

[2] G. L. Clark: X-Ray Metallography in 1929. *Metals and Alloys* (1929) 1, Pt. 1, 14; Pt. 2, 57–68; Pt. 3, 98–111; Pt. 4, 153–161.

Development of Equipment and Tools

The application of radiography to the development of equipment and tools is well illustrated in the development of dies for making aluminum-alloy castings.   Fig. 1 is a radiograph of six plungers for telephone hand-sets made in a double-gated die.   By cutting out one gate so that the metal entered from a single gate, the die filled without entrapping gas. Fig. 2 shows that plungers made in this manner by the same die are much sounder than those made in the die as originally designed.

Radiography Applied to Studies of Materials

One of the more recent uses of radiography has been in the study of dendritic crystallization and like structures in metals and alloys.
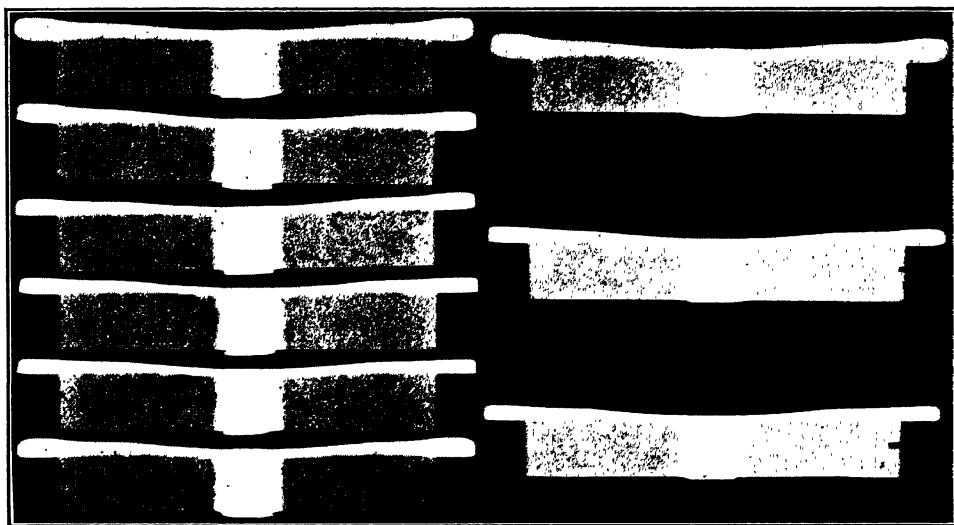
FIG. 1.—PorOUS DIE CASTINGS MADE BY
DOUBLE-GATED DIE.

FIG. 2.—SOUND DIE CASTINGS MADE BY
SINGLE-GATED DIE.

Recently cross-sections of 50 copper wire bars were examined radiographically.   Most of these bars were "level set" according to mill terminology.   For the sake of comparison, the structure shown in Figs. 3 and 4 has been taken as a norm.   The cross-section of such normal bars is composed of a dendritic skin around the mold surfaces, which thins out towards the top of the sides, a zone of equiaxed grains above this in the lower half of the bar, a core of dendritic crystallization at the top center with a zone of segregation of small gas bubbles on each side extending towards the lower part of the bar, and an area of gas segregation

FIG. 4.—SECTION SHOWN IN FIG. 3.   × 1.   ETCHED IN 50 PER CENT. NITRIC ACID.

FIG. 3.—RADIOGRAPH OF ⅜-IN. SECTION OF NORMAL COPPER WIRE BAR.
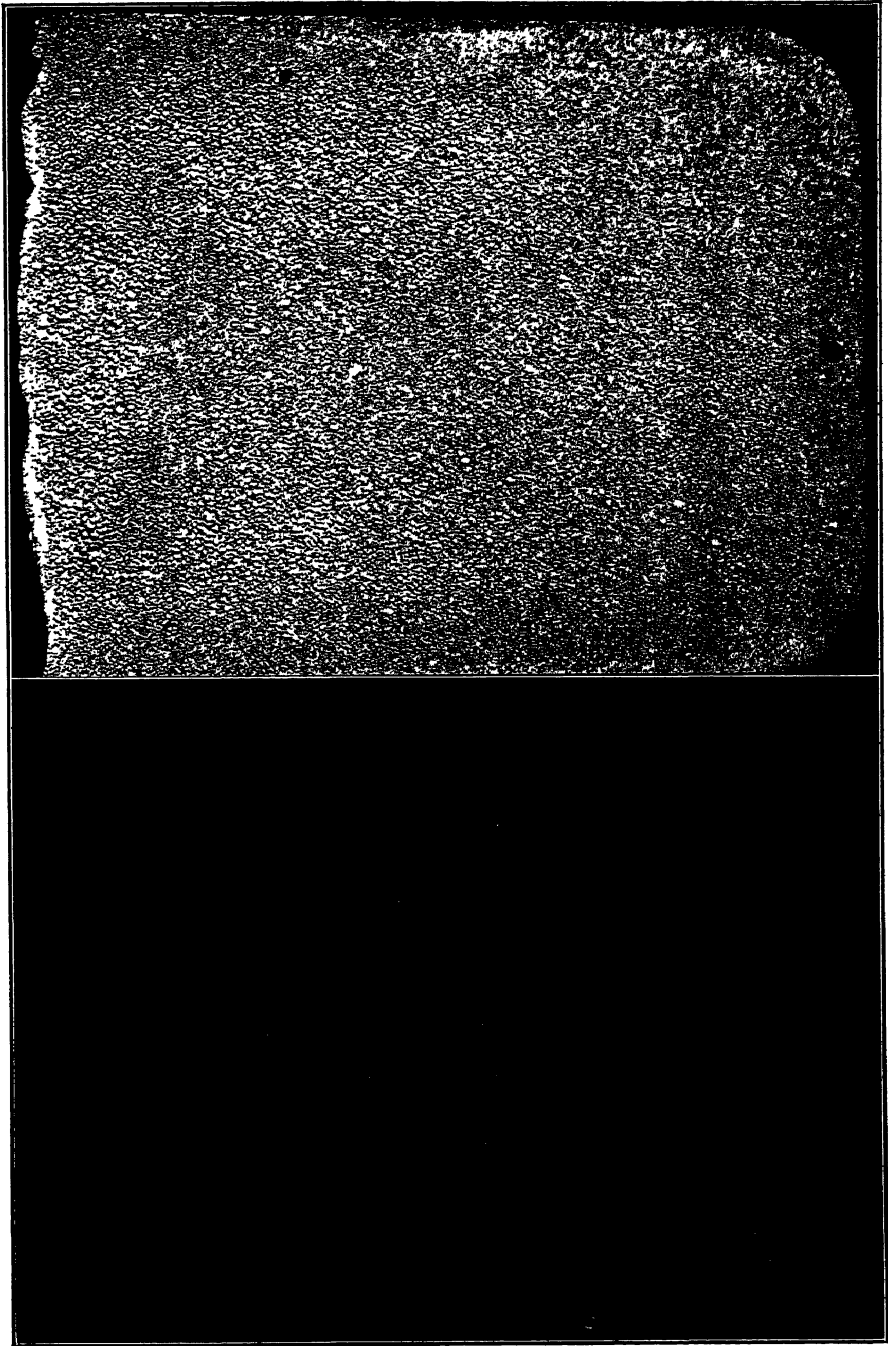
FIG. 5.—RADIOGRAPH OF ⅜-IN. SECTION OF COPPER-WIRE BAR
SHOWING GASSY STRUCTURE.

FIG. 6.—SECTION SHOWN IN FIG. 5. × 1. ETCHED IN 50 PER
CENT. NITRIC ACID.

at the top surface of the bar.   Variations in dendritic structure and three types of discontinuities not present in the normal structure were observed in many bars.

The first of these types of discontinuity is due to the segregation of gas (Figs. 5 and 6).   Large gas pockets are distributed throughout the cross-section, and the bar is almost wholly made up of equiaxed grains.
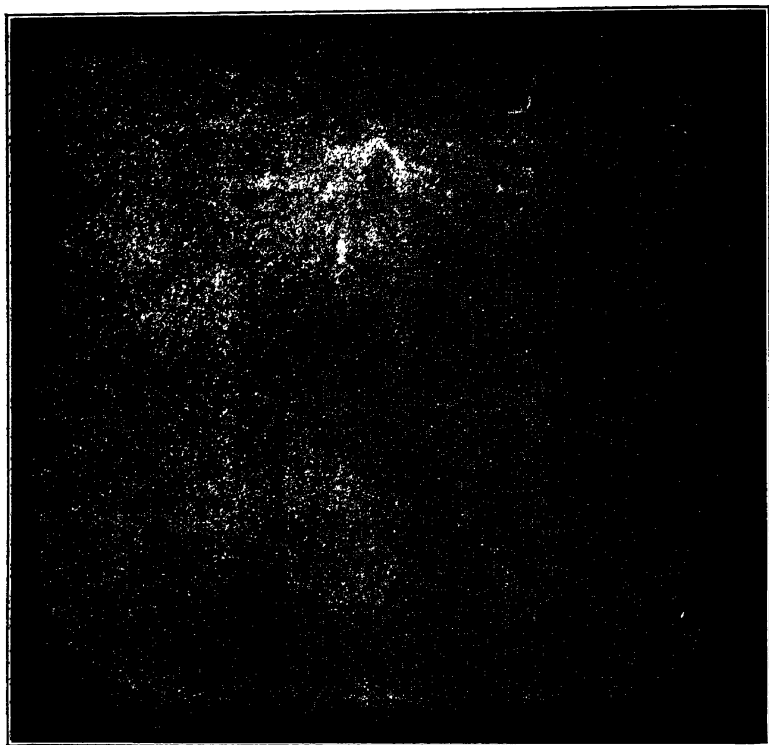
FIG. 7.—RADIOGRAPH OF ⅜-IN. SECTION OF COPPER WIRE BAR SHOWING DISCONTINUITY FOLLOWING CONTOUR OF BAR.

No dendritic skin or core is evident.   The gas appears to have been entrapped before it had time to rise to the surface of the bar.   This structure might be due either to the effect of the gas on the crystallization habit of copper or to the rapid solidification of the ingot from a temperature just above the freezing point of copper and from a very large number of nuclei.

Fig. 7 shows a typical example of a second type of discontinuity. This is characterized in the radiograph by the appearance of a light line following the contour of the mold surface.   Inside the line of discon-
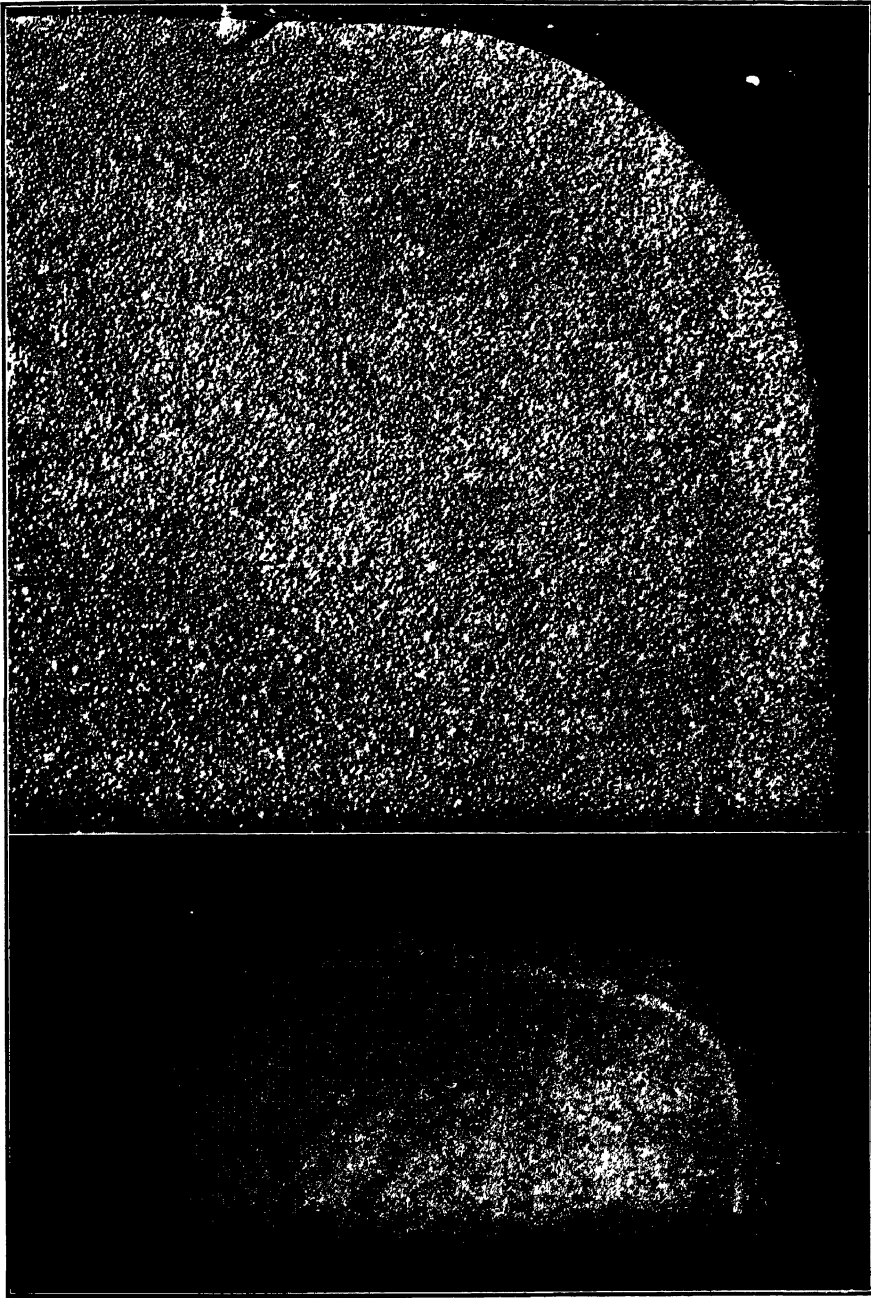
FIG. 9.—SECTION SHOWN IN FIG. 8. × 3. ETCHED IN 50 PER CENT. NITRIC ACID.

FIG. 8.—RADIOGRAPH OF SECTION OF COP- PER WIRE BAR SHOWING TWO LINES OF DIS- CONTINUITY FOLLOWING CONTOUR OF BAR.

tinuity numerous gas bubbles are uniformly distributed in the lower portion of the bar. The top exhibits about the same structure with slightly more gas than is shown by the normal bar of Fig. 3. Sometimes two parallel lines of discontinuity are observed, as in Fig. 8. In this type, if there is a dendritic shell, the dendrites stop at the line of discontinuity. Fig. 9 is a macrograph of a portion of the section radiographed in Fig. 8. The two light lines of the radiograph appear in the etched section as lines distinguishable from the groundmass because of the absence of gas bubbles. These lines may be due to a hard mechanical shock delivered to the bar during solidification. If the bars were poured in a rotary mold system, such a shock might be delivered to the rest of the train when each bar is dumped. The effect on the bars would depend upon the stage of partial crystallization in each case. If only the first dendrites had formed, the bubbles of gas might be jarred out of the area just above the dendritic skin. Crystallization would then progress in the usual way, entrapping gas bubbles, but a line free from gas would remain, which, being denser than adjacent areas, would absorb more of the X-ray beam and appear in the radiograph as a light line. Should two shocks occur coincident with the proper stages of crystallization in the same bar, two such lines would be formed, as in Fig. 8.

A third type of discontinuity is illustrated in Figs. 10 and 11. There are evident in the radiograph a series of light and dark bands and lines around the mold surfaces. These pass directly through the dendrites of the dendritic skin. The dendrites of this skin are long, the zone of equiaxed grains at the bottom of the bar is narrow, the dendritic core is very long, as are also the areas of gas segregation on either side of it, and the top of the bar is particularly gassy. The bar is not of normal shape in that it is smashed over at the top towards the right in the radiographed section. These facts indicate that the bar was cast at a relatively high temperature and was dumped just before complete solidification had taken place, thus causing the inner part of the bar to pull away from the outer part.

Whatever has been said above regarding the interpretation of these structures is tentative, for work in this field has just begun and so far we have had no opportunity to synthesize these structures under controlled conditions. The radiographs presented have shown conclusively that the external appearance of the bar is no criterion of its internal structure except when the bar is misshapen as in Fig. 10. Whether the four types of bars discussed are equally good for the production of wire is yet to be determined.

The types of discontinuities that have been mentioned may persist after the material is rolled into rod. This is illustrated by Fig. 12, which is a radiograph of a wire bar having a long dendritic core with areas of gas
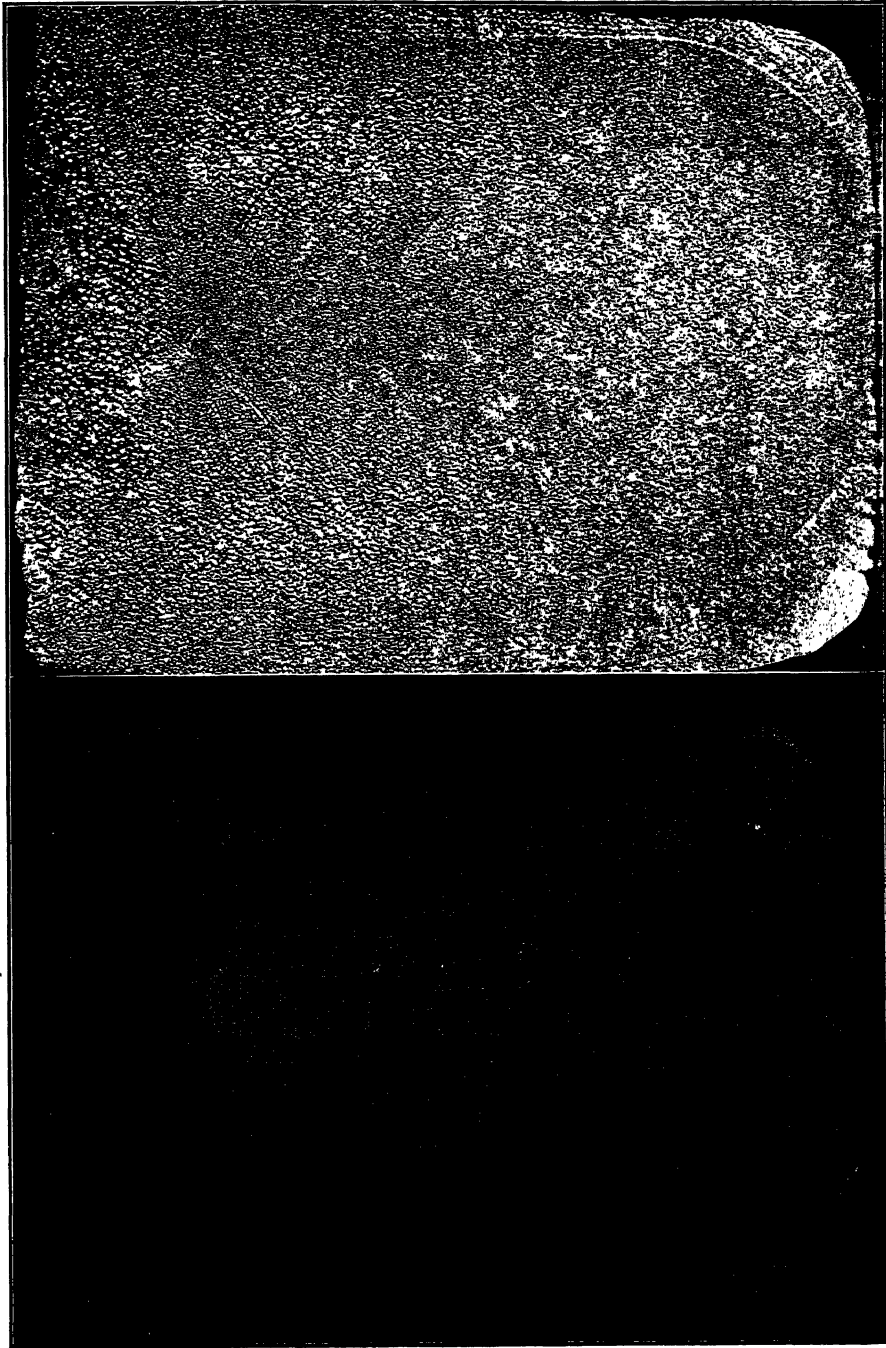
FIG. 10.—RADIOGRAPH OF ⅜-IN. SECTION OF COPPER WIRE BAR SHOWING DISCONTINUITY PASSING THROUGH DENDRITIC SKIN OF BAR.

FIG. 11.—SECTION SHOWN IN FIG. 10. ETCHED IN 50 PER CENT. NITRIC ACID.

segregation on either side and below the core, and by Fig. 13, which shows an etched section of the first roughing-mill pass of this bar rolled at 1500° F.   First pass sections of other bars rolled at the usual temperature also showed this structure.   Sections of rod taken on the same day on which those of Figs. 12 and 13 were rolled show the cored structure when etched (Fig. 14).
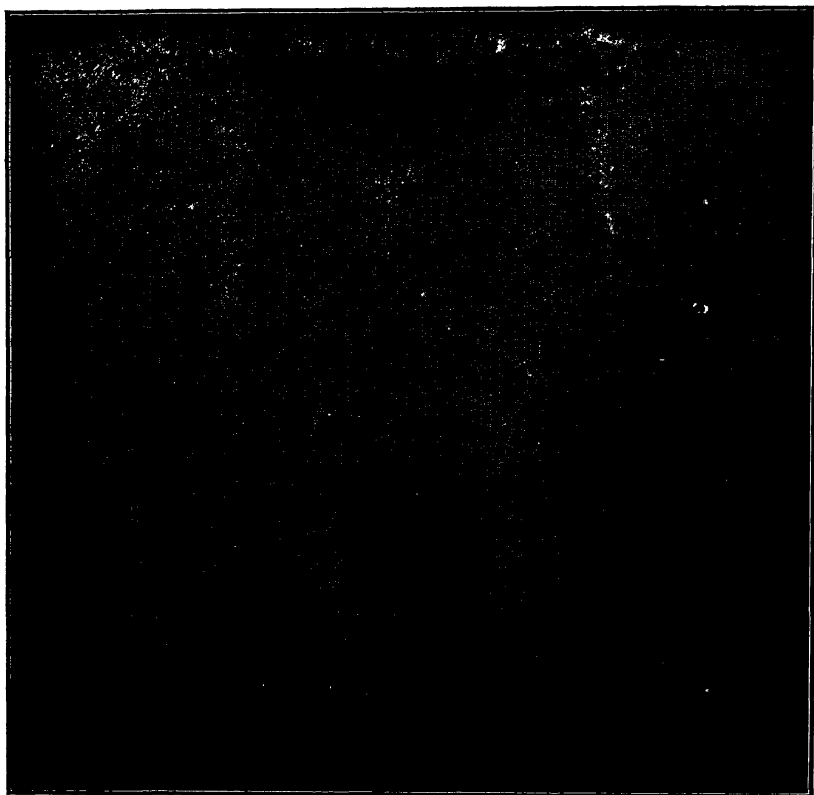
FIG. 12.—RADIOGRAPH OF COPPER WIRE BAR SHOWING LONG DENDRITIC CORE.

X-RAY DIFFRACTION PATTERNS

Besides radiography, the many types of diffraction patterns are of prime importance in the study of materials.

As an example of the use of X-ray diffraction in the study of materials, consider two samples of tin-coated copper condenser foil, one of which was hot-dipped and the other electroplated.   When condensers made from the two samples were subjected to a laboratory aging test— which consists, in general, of measuring the capacity of the condensers upon application and release of mechanical pressure at different tempera-

FIG. 13.—SECTION OF FIRST PASS OF WIRE BAR SHOWN IN FIG. 12.   × 1.5.   BAR WAS
ROLLED AT 1500° F.   ETCHED IN 50 PER CENT. NITRIC ACID.

tures—it was observed that the capacity of condensers made from the hot-dipped stock did not return to the original value in conclusion of the
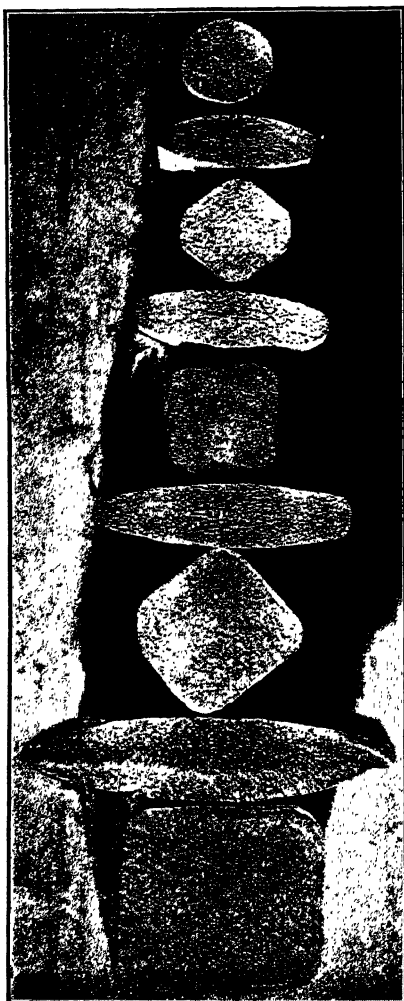
FIG. 14.—SECTIONS OF ROD ROLLED ON SAME DAY AS BAR SHOWN IN FIG. 12.   × 1.5.   ETCHED IN 50 PER CENT. NITRIC ACID.
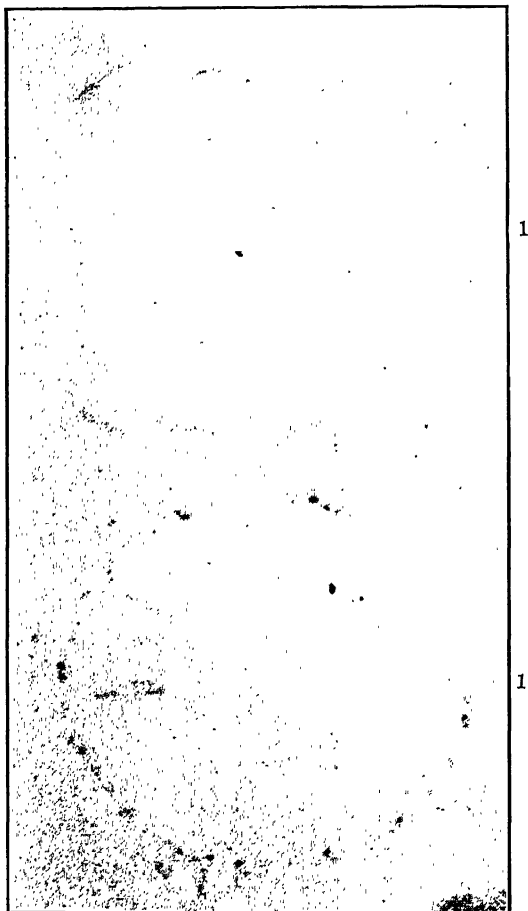
FIG. 15.—DIFFRACTION   PATTERN   OF 0.001-IN. COPPER CONDENSER FOIL AFTER STRIPPING OFF ELECTROPLATED TIN COATING.
FIG.   16.—DIFFRACTION   PATTERN   OF 0.001-IN. COPPER CONDENSER FOIL AFTER STRIPPING OFF HOT-DIPPED TIN COATING.

test, while that of condensers from the electroplated stock did.   Both stocks were supposedly on an annealed copper base.   Pinhole diffraction patterns showed, as illustrated in Figs. 15 and 16, that the copper base

of the electroplated sample was annealed while that of the hot-dipped sample was cold-worked. This type of diffraction pattern can be made by an overnight exposure with the expenditure of about ½ hr. of an engineer's time. Taking photomicrographs of the same samples requires considerably more time.

THE FIELD OF X-RAY METALLOGRAPHY

From these examples, it is evident that the use of X-rays makes possible the study of features of metals and alloys in a way not possible by other metallographic methods. In radiography X-rays are used to integrate solid sections in one plane, or, aided by the stereoscope, to see the extent and direction of defects in three dimensions. This gives more knowledge than the usual method of sectioning and etching in the study of such features as gas bubbles, shrinks, cracks and other discontinuities. At present, however, the cost is prohibitive except in development work or unless the engineering requirements for the casting or forging are unusual.

DISCUSSION

(W. R. Webster presiding)

J. W. SCOTT, Chicago, Ill. (written discussion).—This paper illustrates the value of new laboratory technique in assisting to improve and to maintain already existing high efficiency in operating metallurgical processes. The radiographs of the copper wire-bar sections cited verify the crystal structure revealed by the corresponding macrographs. In addition, they show more clearly than the macrographs the gas concentration and high-density areas.

Recently an experiment was made at the Hawthorne copper refinery to increase the density of tough-pitch copper wire bars by adopting the ingot-shaker principle used in the ferrous industry—that is, by continually jarring the mold while the molten metal is solidifying. Radiographs indicating the effectiveness of the operation are shown in Figs. 17 and 18. Fig. 17 is a section of a commercial copper wire bar cast normally with no jarring of the mold during solidification. Fig. 18 is a section of a bar cast from the same heat of copper within a few seconds time of the first bar, but with the mold jarred continually by hammering upon it during the solidification period. The effect of the jarring is apparent. It has caused the release and agglomeration of considerable gas, but the gas has not escaped from the bar because the top crust has formed, as usually happens with open-mold castings, before the remainder of the bar has completely solidified. Indications from the radiographs are that the principles of casting ferrous and nonferrous metals are not very different. The radiographs of Figs. 17 and 18 were exposed by Miss Baeyertz.

W. R. WEBSTER, Bridgeport, Conn.—Some years ago we conceived the idea of shaking a mold. We got a large jolt molding machine from the foundry, set up our mold on that, set the machine at work and poured in the metal. I am sorry to say that the result was mostly solidified froth. Possibly with pure copper jarring may improve the casting.

P. A. E. ARMSTRONG, New York, N. Y.—I am forced to agree with Mr. Webster's suggestion that jarring will set up froth in an ingot mold and instead of imparting solidity to an ingot actually will add to the cavities so much so that the ingot is apt to be principally holes.   However, there are ways to jar and ways not to jar.   If the ingot mold is given a rotary motion and made to oscillate with a quick snap to the motion in one direction, the jarring will cause solidity in the ingot and will cut out any tendency towards frothing.   A simple experiment with sand in a glass vessel will demonstrate how well a quickly reciprocating circular motion will cause the sand to pack down, whereas an up-and-down motion will not have the same effect.   I understand that the type of jarring I refer to has been tried out both on a small and large ingot scale and has been found to be successful in both instances.

W. R. WEBSTER.—That practice has been followed in tube casting, by rotating the molds, for a number of years.   I believe it is an old process.
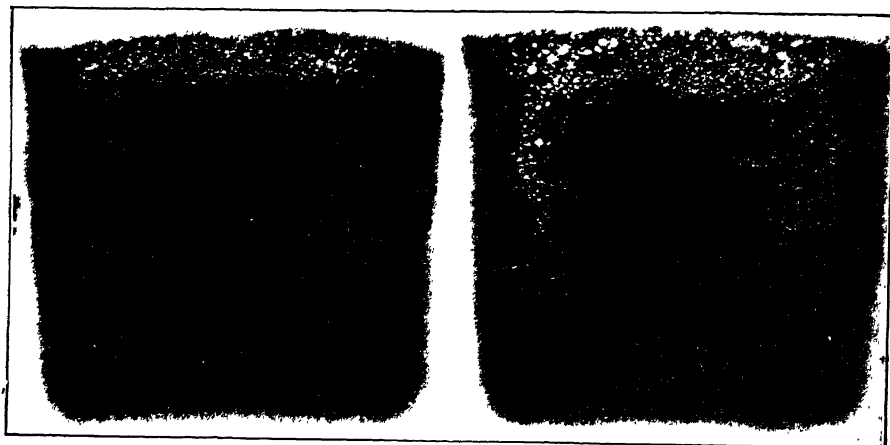
FIG. 17.   FIG. 18.

FIG. 17.—RADIOGRAPH OF COPPER WIRE BAR FROM MOLD THAT WAS NOT JARRED.
FIG. 18.—RADIOGRAPH OF COPPER WIRE BAR FROM MOLD THAT WAS JARRED CONTINUALLY.

L. W. MCKEEHAN, New Haven, Conn. (written discussion).—The radiographs shown by Dr. Baeyertz are good examples of what may be done in the study of relatively small metal parts and sections of heavy pieces.   However, the X-ray tests of copper wire bars were not "nondestructive," since complete slices had to be cut from the bars for these photographs.   The advantage gained by the radiographic method is that the quality for a length equal to the thickness of the slice—here $\frac{3}{8}$ in.—is obtained at one operation, whereas a polished surface shows only what lies in a single cross-section.   I would be interested to learn what degree of smoothness in the surfaces of the slice was necessary, since even slight scratches will show in a radiograph of this sort.   The diffraction patterns are interesting, but here show only major differences in character of metal.   The studies of preferred orientation and its effect upon working properties in sheet materials have been much more extensive in other laboratories.

M. BAEYERTZ (written discussion).—Although the radiographs of copper wire bars required cutting sections from the bars, it is difficult to see how such information·

could be obtained otherwise since present equipment for the generation of X-rays does not permit the penetration of $3\frac{1}{2}$ to 4 in. of copper necessary to radiograph the total thickness of a wire bar with a reasonable time of exposure. The sections of wire bar were surfaced with a milling cutter or turned down on a lathe. The diffraction patterns contained in this paper cannot fairly be construed in the class "studies of preferred orientation and its effect upon working properties in sheet materials." This section of the paper is merely an illustration of the facility with which the physical state of such materials—purchased industrial materials—can be determined by means of diffraction patterns.

Thermal Conductivity of Copper Alloys
II.—Copper-tin Alloys
III.—Copper-phosphorus Alloys

By Cyril Stanley Smith,* Waterbury, Conn.

(Chicago Meeting, September, 1930)

The following table, which is composed of data given in the author's first paper on the thermal conductivity of copper alloys[1], contains the results which have been obtained by previous workers on the thermal conductivity of the copper-tin, the copper-phosphorus and the copper-tin-phosphorus alloys (the phosphor bronzes).

TABLE 1.—*Previous Investigations*

Investigator	Composition, Per Cent. by Weight			Thermal Conductivity, Cal./Sq. Cm./Cm./Sec. °C
	Copper	Tin	Phosphorus	
Hardebeck[a]	95.0	5.0		0.176 (20° C.)
Grossmann[b]	90.1	9.9		0.105 ⎫
	75.5	24.5		0.059 ⎪
	24.9	75.1		0.139 ⎬ (13° C.)
	9.7	90.3		0.131 ⎪
	0.0	100.0		0.142 ⎭
Griffiths and Schofield[c]	91.7	8.0	0.30	0.108 ⎫
	87.2	12.4	0.40	0.087 ⎬ (20° C.)
	90.0	10.0	Small amt.	0.100 ⎭
Donaldson[d]	87.8	11.3	0.35	0.128
Pfleiderer[e]	99.4		0.63	0.250 ⎫ (30° C.)
	98.0		1.98	0.125 ⎭

[a] Dr. Ing. Diss., Aachen, 1909. Quoted by Schenk: *Ann. der Phys.* (1910) **32**, 261.
[b] *Beibl. Ann. der Phys.* (1905) **29**, 178.
[c] *Jnl.* Inst. Metals (1928) **39**, 375.
[d] *Jnl.* Inst. Metals (1925) **34**, 43.
[e] *Ges. Abhand. Kennt. Kohle* (1919) **4**, 409.

Experimental Methods

Since the method of obtaining measurements of the thermal conductivity was identical with that described in the author's previous paper

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* Research Laboratory, American Brass Co.
[1] C. S. Smith: *Trans.* A. I. M. E., Inst. Met. Div. (1930) 84.

it needs no further description here.   The thermocouples were recalibrated several times and found to be holding their original calibration very closely.   The first differential couple was accidentally destroyed and a new one was constructed and calibrated with the same care.

PREPARATION OF MATERIAL

The alloys in the copper-tin series with more than 2 per cent. tin were obtained from stock of the American Brass Co. and are representative high-grade commercial material.   In all cases a small amount of phosphorus was present.   The alloys with 1 and 2 per cent. tin were cast in the laboratory in a mold of 2¼ in. dia.   The bars were cold-rolled with the necessary intermediate annealing down to ⅜ in. dia. where they were annealed at 650° C. for 30 min. and slowly cooled before the conductivity test pieces were machined.

The copper-phosphorus alloys were all cast in the laboratory and treated similarly.   The final anneal was at 650° C. for 1 hr., followed by cooling in air.   The additions of phosphorus were made as commercial 15 per cent. phosphor copper of high purity.   Table 2 gives the complete analyses of the various bars.

TABLE 2.—Analyses of Alloys Used

Bar No.	Composition, Per Cent. by Weight					
	Copper	Tin	Phosphorus	Iron	Lead	Oxygen
2	99.986			0.0016		0.022
74	99.00	0.99	0.002	0.01	0.00	
75	98.09	1.92	0.01	0.01	.0.00	
41	94.86	4.92	0.06	0.05	0.01	
43	92.55	7.48	0.04	0.02	0.01	
44	89.52	10.40	0.03	0.05	0.01	
40	95.56	4.18	0.33	0.01	0.04	
42	94.02	4.88	0.06	0.03	1.16	
93	99.94		0.042	0.004		
82	99.97		0.075	0.04		
95	99.74		0.187			
83	99.53		0.480	0.05		
94	99.31		0.677	0.002		
84	99.12		0.930	0.06		

The range of composition of the copper-tin alloys was limited to the useful alloys in the alpha solid solution range.   The limit of solubility is 16 per cent. at 520° C. and between 14 and 15 per cent. at room temperatures, according to Haughton[2], Hansen[3] and Carson[4], but under conditions

[2] J. L. Haughton: *Jnl.* Inst. Met. (1925) **34**, 121.
[3] M. Hansen: *Ztsch. f. Metallkunde* (1927) **19**, 407.
[4] O. A. Carson: *Canadian Inst. Min. and Met. Bull.* 201, (1929) 129.

which do not approach equilibrium the apparent solubility will be much less than this and commercial malleable alloys are limited to about 10.5 per cent. tin, which was the highest amount of tin in the present series.

In the copper-phosphorus system the limit of solubility, which is about 1.1 per cent. at 750° C., according to Hanson, Archbutt and Ford[5], drops to 0.5 per cent. at 400° C. and becomes slightly lower at room temperatures. At 650° C., the temperature at which the conductivity test pieces were annealed, the solubility is about 0.9 per cent.

The results of the determinations are given in detail in Tables 3 and 4, and are plotted in Figs. 1 to 4.

TABLE 3.—*Thermal Conductivity of Copper-tin Alloys*

Bar No.	Tin, Per Cent.	Phosphorus, Per Cent.	Electrical Conductivity λ at 20° C., Ohm^{-1} Cm. $\times 10^{-4}$	Electrical Conductivity at 20° C., Per Cent. I.A.C.S.	Thermal Conductivity at 20° C., Per Cent. of Copper	Thermal Conductivity K at 20° C., Cal./Sq. Cm./Sec./°C.	Thermal Conductivity K at 200° C., Cal./Sq. Cm./Sec./°C.	Temperature Coefficient of Thermal Conductivity α at 20° C.	Wiedemann-Franz Ratio $\frac{K}{\lambda T} \times 10^9$ at 293° Abs.
2	0.0	0.000	58.962	101.66	100.0	0.941	0.934	0.000041	5.45
74	0.99	0.002	31.364	54.07	57.7	0.543	0.616	0.00075	5.91
75	1.92	0.01	21.154	36.47	42.0	0.395	0.481	0.00121	6.37
41	4.92	0.06	10.674	18.40	20.7	0.195	0.264	0.00197	6.24
43	7.48	0.04	7.8945	13.61	16.4	0.154	0.209	0.00201	6.65
44	10.40	0.03	6.4362	11.10	12.9.	0.121	0.171	0.00230	6.31
40	4.18	0.33 Pb	7.3190	12.62	15.9	0.150	0.196	0.00171	6.99
42	4.88	1.16	10.655	18.37	21.2	0.199	0.264	0.00181	6.38

TABLE 4.—*Thermal Conductivity of Copper-phosphorus Alloys*

Bar No.	Phosphorus, Per Cent.	Electrical Conductivity λ at 20° C., Ohm^{-1} om. $\times 10^{-4}$	Electrical Conductivity at 20° C., Per Cent. I.A.C.S.	Thermal Conductivity at 20° C., Per Cent. of Copper	Thermal Conductivity K at 20° C., Cal./Sq. Cm./Sec./°C.	Thermal Conductivity K at 200° C., Cal./Sq. Cm./Sec./°C.	Temperature Coefficient of Thermal Conductivity α at 20° C.	Wiedemann-Franz Ratio $\frac{K}{\lambda T} \times 10^9$ at 293° Abs.
2	0.000	58.962	101.66	100.0	0.941	0.934	0.000041	5.45
93	0.042	43.346	74.72	77.3	0.727	0.791	0.00049	5.74
82	0.075	32.669	56.32	60.4	0.568	0.649	0.00079	5.94
95	0.239	18.430	31.77	36.8	0.346	0.426	0.00128	6.40
83	0.480	11.842	20.42	23.0	0.216	0.299	0.00214	6.23
94	0.677	8.614	14.85	17.5	0.165	0.248	0.00279	6.55
84	0.930	6.5488	11.29	13.7	0.129	0.178	0.00211	6.73

[5] D. Hanson, S. L. Archbutt and G. W. Ford: *Jnl.* Inst. of Met. (1930) **43**, 41; also (abridged) *Engng.* (1930) **129**, 522.

COPPER-TIN SERIES

The addition of tin to copper causes a very rapid decrease of the conductivity, as can be seen in Fig. 1. The curves of the thermal conductivity at 20° and 200° C. become further apart as the tin increases, a fact which is reflected by the temperature coefficient curve, which rises rapidly at first but which later tends to become horizontal.

Fig. 2 shows the electrical and thermal conductivity values at 20° C. plotted against composition, and also the Wiedemann-Franz-Lorenz
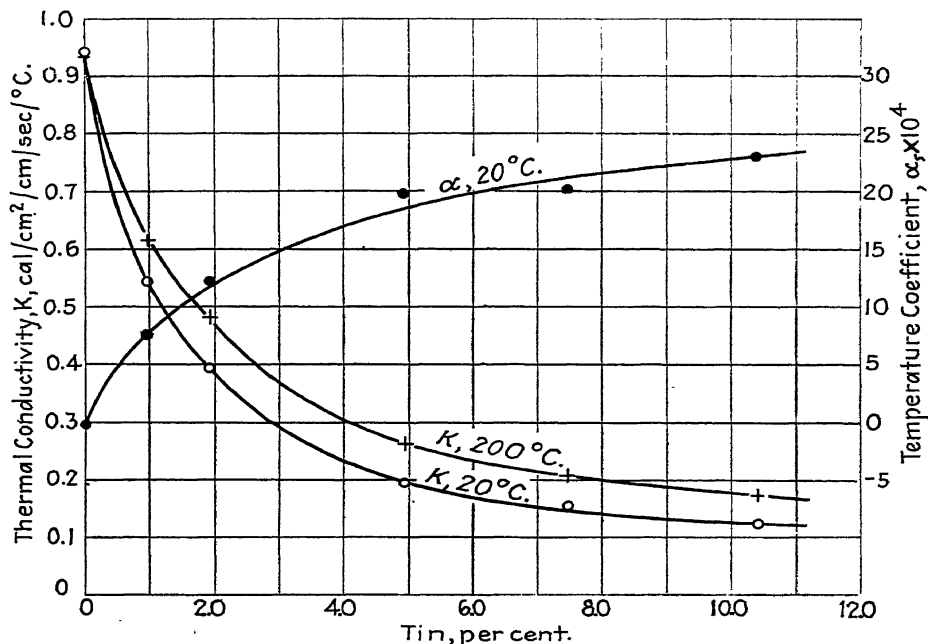
FIG. 1.—THERMAL CONDUCTIVITY OF COPPER-TIN ALLOYS.

coefficient, $\dfrac{K}{\lambda T}$, where K is the thermal conductivity in cal./sq. cm./cm./-sec./° C., λ the electrical conductivity in ohms^{-1} cm. and T the absolute temperature, in this case 293° K. The electrical conductivity in Fig. 2 is expressed as a percentage of the International Annealed Copper Standard, while the thermal conductivity is given as a percentage of the conductivity of the copper used (0.941 cal./sq. cm./cm./sec./° C.). It should be pointed out that since the copper had an electrical conductivity of 101.66 per cent. I. A. C. S., the beginning of the electrical conductivity curve is displaced nearly 1.7 per cent. above that of thermal conductivity, and this must be taken into consideration when comparing the results. In spite of this displacement the thermal conductivity curve rapidly

crosses the other, and for all of the alloys examined the per cent. thermal conductivity is the greater. The Wiedemann-Franz-Lorenz ratio reflects this proportional increase and the curve shows a rapid rise from 5.45×10^{-9} for pure copper to 6.3×10^{-9} for 2.0 per cent. tin, followed by a much smaller increase to about 6.6×10^{-9} at the end of the range studied.

The addition of a third element to the copper-tin alloys was not studied in detail, only two alloys being tested. Bar 40, containing 0.33
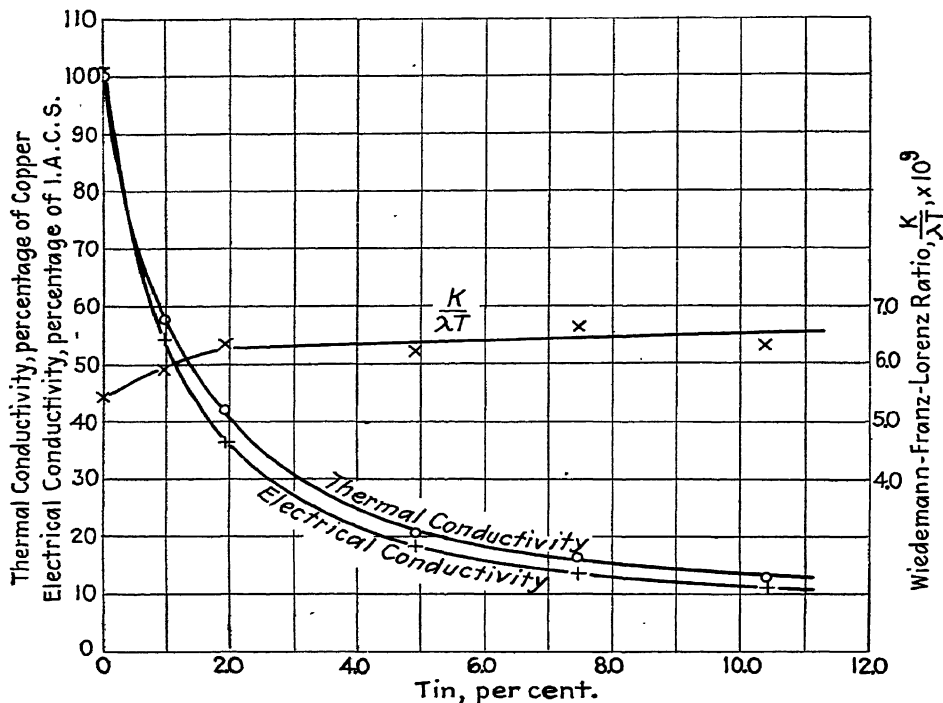
Fig. 2.—Comparison of electrical and thermal conductivity of copper-tin alloys at 20° C.

per cent. phosphorus and 4.18 per cent. tin, has, as would be expected, considerably lower conductivity than the similar alloy without phosphorus. The Wiedemann-Franz-Lorenz ratio is much higher than the binary alloy. Lead, being insoluble, has very little effect on the conductivity, as bar 42 with 1.16 per cent. lead and 4.88 per cent. tin shows. It is almost identical in conductivity with bar 41, a similar alloy with no lead.

Copper-phosphorus Series

The conductivity of the copper-phosphorus series is shown in Figs. 3 and 4. The curves are similar to those of the copper-tin series except

that phosphorus is 10 times as powerful as tin in reducing the conductivity. The temperature coefficient curve rises steeply to beyond 0.7 per cent. and then drops to a smaller value for the sample with 0.93 per cent. phosphorus. The conductivity of the latter bar at 20° C. lies exactly on the curve extrapolated from lower phosphorus contents and only the 200° C. point is affected. The discrepancy is much greater than the experimental error and there is little doubt that the decrease is real. The amount of phosphorus in this bar is a little beyond the solubility limit at the anneal-
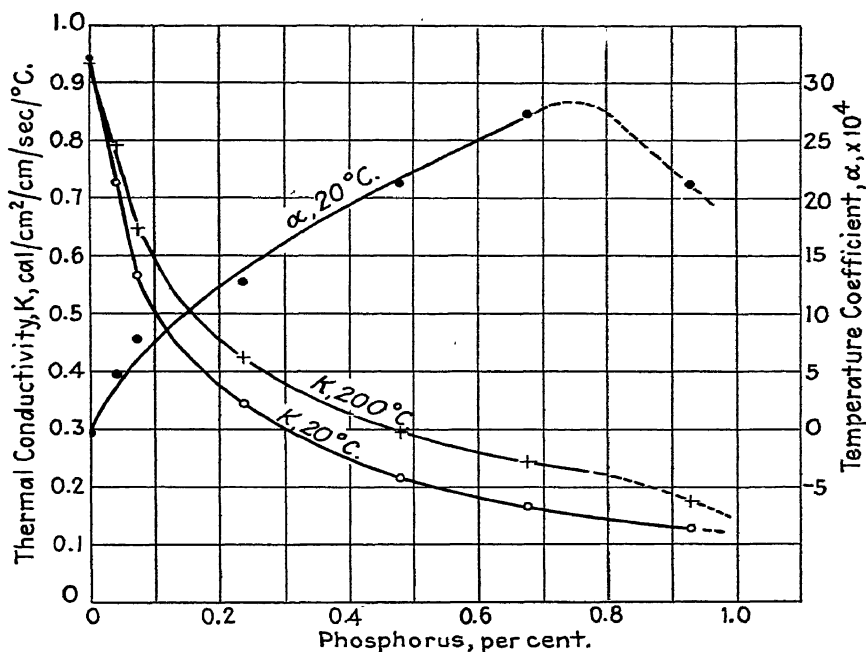
FIG. 3.—THERMAL CONDUCTIVITY OF COPPER-PHOSPHORUS ALLOYS.

ing temperature, 650° C., and considerably beyond it at room temperatures. It is therefore highly probable that the discrepancy is due to the presence of undissolved Cu_3P in the sample and it is very likely that precipitation occurred during cooling after annealing or even during heating for the actual determinations. Microscopic examination showed a number of small particles of Cu_3P but no general precipitation was observed.

Fig. 4 allows direct comparison between the electrical and thermal conductivity of the series. Again there appears an initial rapid increase in the Wiedemann-Franz-Lorenz coefficient, followed by a small linear increase. This has occurred in all the solid solution ranges which have yet been examined and it is evidently of some basic physical significance.

SUMMARY

This paper is a continuation of the work on the thermal conductivity of copper alloys described in the author's previous paper. The thermal conductivity of copper (0.941 cal./sq. cm./cm./sec./° C.) is rapidly reduced by the addition of tin until with 10.41 per cent. tin it is only 0.121 cal./sq. cm./cm./sec./° C. at 20°C. Phosphorus is 10 times as powerful as tin, as little as 0.93 per cent. phosphorus reducing the conductivity to
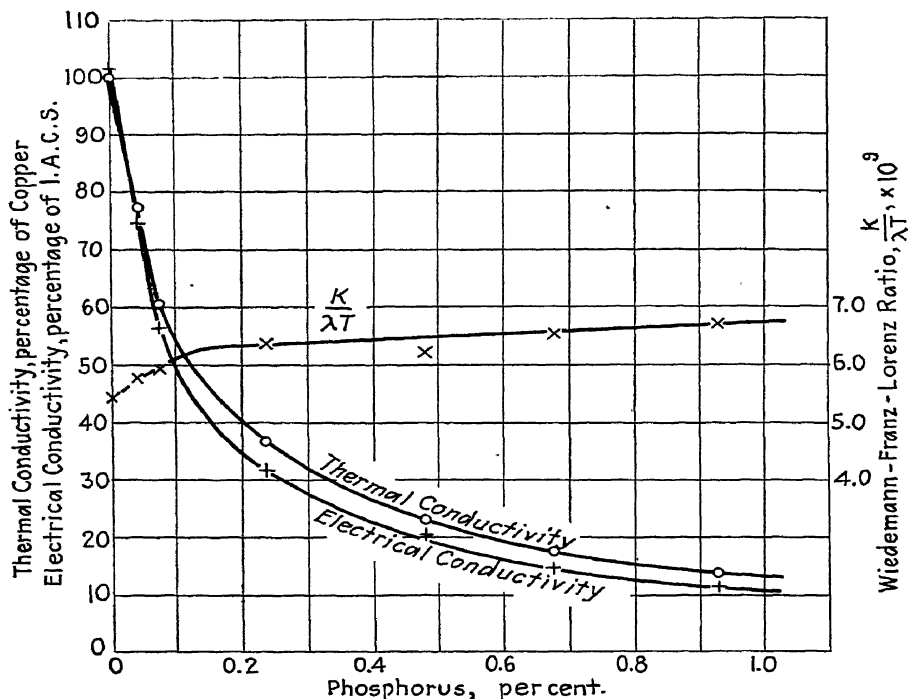
FIG. 4.—COMPARISON OF ELECTRICAL AND THERMAL CONDUCTIVITY OF COPPER-PHOSPHORUS ALLOYS AT 20° C.

0.129 cal./sq. cm./cm./sec./° C. The electrical conductivity decreases more rapidly on alloying than does the thermal conductivity, and the Wiedemann-Franz-Lorenz ratio increases rapidly at first, but beyond 2.0 per cent. tin or 0.15 per cent. phosphorus remains almost constant. This break in the Wiedemann-Franz-Lorenz ratio curve has occurred in every system yet examined and is evidently. of basic physical significance.

of the American Brass Co. at Ansonia, Conn., and the author wishes to express his thanks to Mr. Schmid for his help in this connection. The assistance of Mr. E. L. Munson, who determined the thermal conductivity of several of the bars in the present series, is also gratefully acknowledged. The chemical analyses were performed in the chemical laboratory of the American Brass Co. under the direction of Mr. C. H. Davis, and the author especially wishes to thank those who took part in this work. Finally, no paper from the laboratory of the American Brass Co. would be complete without some reference to the encouragement and inspiration obtained from contact and conversation with Mr. W. H. Bassett, whose interest and general supervision has done much to further the work described in this paper.

APPENDIX

INDIVIDUAL EXPERIMENTAL VALUES OBTAINED ON EACH BAR

BAR 74, 0.99 PER CENT. SN, 0.002 PER CENT. P		BAR 75, 1.92 PER CENT. SN, 0.01 PER CENT. P		BAR 41, 4.92 PER CENT. SN, 0.06 PER CENT. P		BAR 43, 7.48 PER CENT. SN, 0.04 PER CENT. P	
°C.	K	°C.	K	°C.	K	°C.	K
234	0.629	230	0.497	238	0.277	238	0.218
232	0.635	227	0.492	237	0.282	236	0.219
180	0.606	206	0.482	180	0.255	235	0.220
177	0.609	174	0.470	179	0.258	182	0.203
129	0.583	172	0.466	130	0.236	181	0.203
127	0.584	156	0.459	129	0.239	180	0.205
83	0.564	123	0.447	87	0.215	133	0.189
83	0.564	122	0.442	87	0.220	132	0.190
67	0.563	110	0.438	69	0.211	131	0.191
67	0.561			68	0.216	97	0.179
51	0.560			51	0.208	96	0.182
51	0.557			50	0.213	77	0.171
						76	0.171
						59	0.164
						58	0.162

BAR 44, 10.40 PER CENT. SN, 0.03 PER CENT. P		BAR 40, 4.18 PER CENT. SN, 0.33 PER CENT. P		BAR 42, 4.88 PER CENT. SN, 1.16 PER CENT. PB		BAR 93, 0.042 PER CENT. P	
°C.	K	°C.	K	°C.	K	°C.	K
289	0.179	241	0.207	239	0.279	204	0.791
239	0.184	241	0.206	239	0.280	203	0.796
180	0.163	183	0.191	181	0.258	157	0.774
179	0.168	181	0.190	181	0.257	156	0.777
130	0.150	132	0.179	131	0.240	113	0.758
128	0.155	131	0.176	131	0.239	112	0.760
87	0.137	96	0.166	88	0.220	64	0.745
68	0.134	77	0.164	87	0.225	64	0.743
50	0.132	58	0.162	86	0.224	64	0.740
				69	0.213		
				69	0.218		
				68	0.217		
				52	0.207		
				51	0.212		
				51	0.211		

ture and vice versa. In this case, therefore, part of the system behaves as if it were in a state of nonvariant equilibrium and we can legitimately infer the presence of three phases or a phasial reaction (probably peritectic reaction). Since the melt is homogeneous, there must be two solid phases present. Yet the system microscopically shows a continuous series of solid solutions—at least, by ordinary etching reagents. The existence of two series of solid solutions is, therefore, possible and is not to be discounted without careful investigation, preferably by means of X-ray crystal analysis.

Smith has studied the thermoelectric power of Sb-Bi alloys[4] and found a maximum point (not sharp) at about 25 atomic per cent. Sb. The
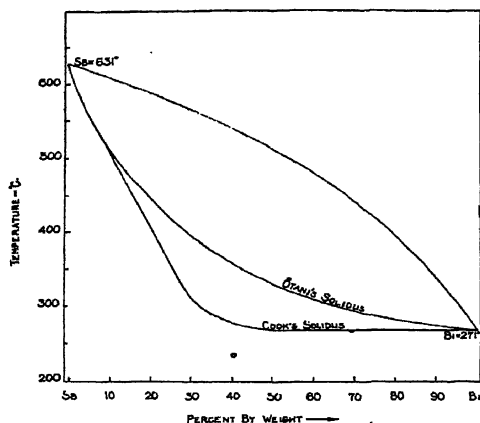
FIG. 1.—CONSTITUTIONAL DIAGRAM OF SYSTEM ANTIMONY-BISMUTH.

Note temperature horizontal from about 48 per cent. Bi to pure Bi, indicating state of *nonvariant* equilibrium, which is contrary to the phase rule. Ōtani's solidus, obtained by resistance method (heating up), is characteristic of a completely isomorphous system. As will be shown later, it represents almost true equilibrium.

resistance shows a corresponding minimum point. (Generally, the presence of an intermetallic compound would show a corresponding increase in the resistance.) Normally, from the general behavior of completely isomorphous systems, we should expect the maximum and minimum properties to be at 50 atomic per cent. The writer's investigation reveals the normal maximum at that point, which suggests that probably Smith's samples were not properly annealed. The writer found that the breaks in his "thermoelectric versus temperature" curves were located higher than in Cook's solidus. A search in the literature showed that Ōtani[5] had already redetermined the solidus by the resistance method

[4] A. W. Smith: The Hall Effect and Some Allied Effects in Alloys. *Phys. Rev.* (1911) **32**, 178.

[5] B Otani: On the Equilibrium Diagram of the Binary Alloys of Antimony and Bismuth. *Sci. Repts.*, Tôkoku Imp. Univ. (1924-5 **13**, 293.

and found it to be the normal solidus of a completely isomorphous system. (See Fig. 1 also.)   Ôtani, however, did not advance any reason for the Cook solidus, which is normally observed by cooling-curve methods, and the writer obtained some interesting results from thermoelectric curves, which, in the light of subsequent thermodynamic evidence, can now be consistently evaluated.

EQUILIBRIA OF ANTIMONY-BISMUTH SYSTEM FROM STANDPOINT OF IDEAL SOLUTIONS

The thermodynamic method of investigating the nature and degree of inner equilibrium offers us a direct means of gaining an insight into the processes occurring within the solution in the course of solidification. The writer has shown elsewhere[6] the development of certain thermodynamic laws of ideal solutions, which appear to apply surprisingly well to metallic systems.   For an ideal solid solution showing either complete or incomplete miscibility, we have

$$\log_{10}\left(\frac{x'_L}{x_S}\right) = \frac{L_F}{2.3R}\left(\frac{1}{T_{F_o}} - \frac{1}{T'}\right) = -\frac{L'_F}{4.58T'} + \frac{L_{F_o}}{4.58T_{F_o}} \qquad [1]$$

in which (x_L'/x_S') represents the ratio of molal concentration of the solvent in the liquid phase to that in the solid in equilibrium with it at any temperature, T'; L_F, the mean molal heat of fusion of the solvent between its melting point, T_{F_o} and T'. As a matter of fact, in the process of integration of the van't Hoff reaction isochore, the heat of fusion is assumed to be constant, but actually it differs in accordance with the change in the specific heat of the melt in equilibrium with the solid. Since the right-hand side of equation 1 is a constant, if we plot log (x_L'/x_S') against $1/T'$, we should obtain a straight line if the system behaves as an ideal solution. As the various assumptions made in deriving equation 1 have been discussed in *Technical Publication* 381, we shall not repeat them here.

Taking points from Fig. 1 (using Ôtani's solidus) and plotting their corresponding log (x_L'/x_S') in terms of molal concentrations of bismuth and antimony, against $10^3/T'$, we obtain Fig. 2.   It is interesting to note that in the range of higher temperatures the system behaves as a truly ideal solution, and the heats of fusion of both bismuth and antimony remain fairly constant (Table 1).   It remains to ascertain the cause of the deviation of *f-e* from the ideal condition represented by the straight line No. 1 in Fig. 2.   In order that we may correctly visualize the behavior of the system, the diagram in Fig. 3 is expressed in mol per cent. Bi. A simple calculation shows that if we assume bismuth to form molecular complexes or polymers, the solidus will become more and more concave downward—that is, the molal concentration of bismuth in the system

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[6] Yap, Chu-Phay: *Op. cit.*
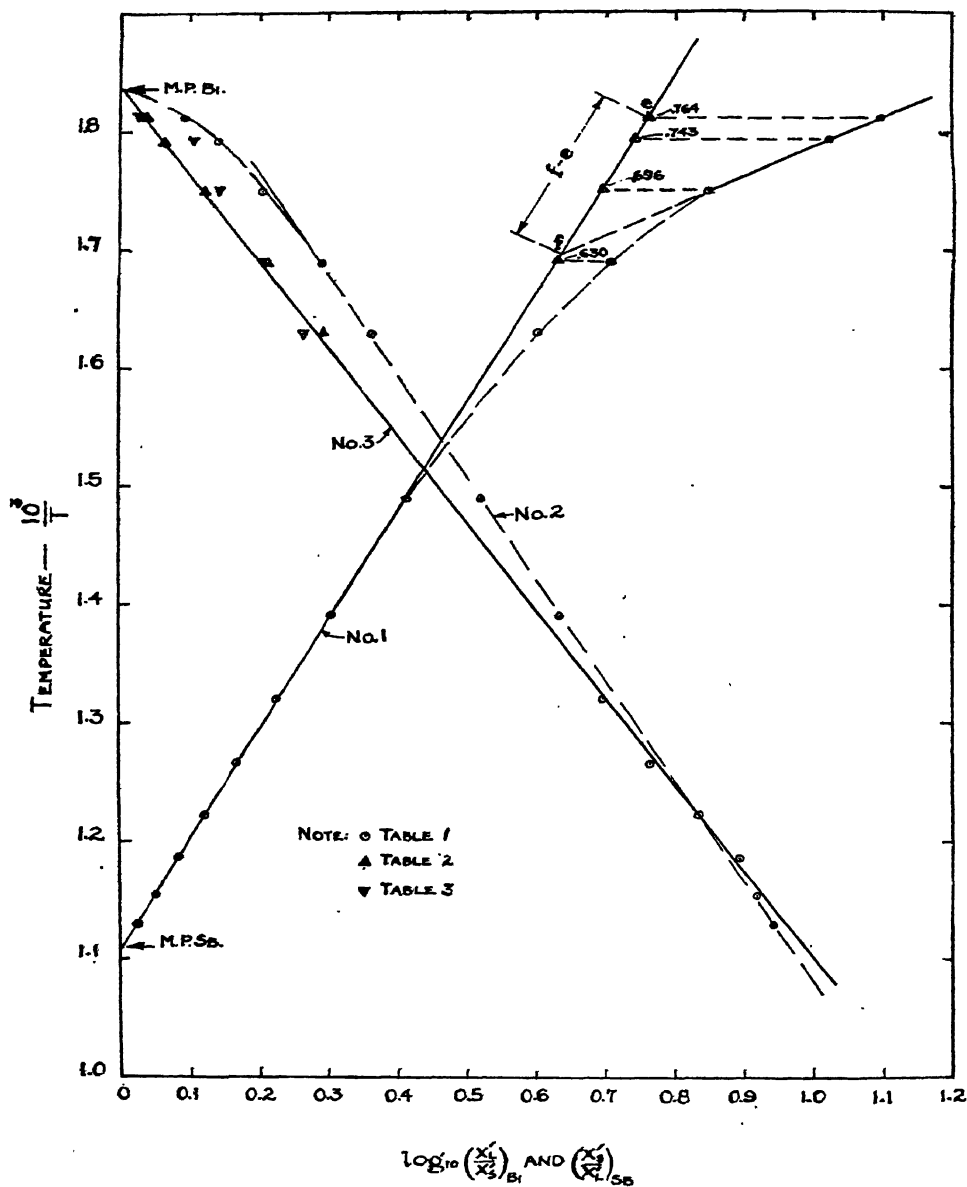
FIG. 2.—IDEALITY OF ANTIMONY AND BISMUTH SOLID SOLUTIONS AS INFERRED FROM FREEZING-POINT BEHAVIOR IN ACCORD WITH THERMODYNAMIC LAWS OF SOLUTION. (SEE EQUATION 1.)

for any definite temperature will be shifted towards the left, as its equivalent molal concentration will be less. Note that in Fig. 2 the alloys 11 to 13 deviate from the straight line No. 1 so as to form a straight line. This is strong presumptive evidence that in that range there must have occurred a definite (and completed) change in the mol number of one of the constituents. Since there is practically no disagreement regarding the liquidus, the change must occur, therefore, in the solid solution (along the solidus). Also any break in the liquidus would be immediately noticeable on account of its steep slope, while this is not true of the solidus, as will be apparent from a study of Fig. 4.
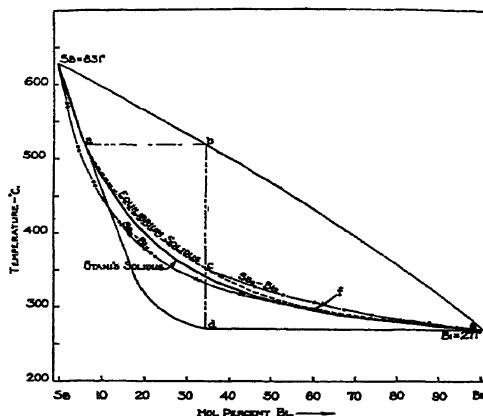
FIG. 3.—CONSTITUTIONAL DIAGRAM EXPRESSED IN MOL PER CENT. BL
   Curves calculated on assumption that all antimony is diatomic (Sb₂) in equilibrium with Bi₂ and Bi₃. Note relation *abcd*. This diagram should be studied in conjunction with Fig. 4.

From the slope of the log $(x_L'/x_S')T^{-1}$ lines of Sb and Bi (1 and 2 in Fig. 2) we calculate roughly the heat of fusion to be around 40 and 26.4 cal. per gram respectively. If we consider bismuth to be diatomic, as its heat of fusion is reported to be about 10 to 17 cal. per gram, we are forced to conclude that antimony must also be diatomic,[7] because otherwise there will be a great change in all the calculated mol fractions of antimony in the system, thus materially affecting the calculated heat of fusion of both metals. Assuming for the moment, then, that antimony is diatomic, like bismuth, the mol fractions of Bi₂ in alloys 10 to 13 are recalculated on the basis of their logarithm values on line 1 (Fig. 2). The new logarithm values are obtained simply by reading off on line 1 the horizontal projections of the observed values on that line. These new values (Table 2) may be interpreted as real equilibrium values.

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[7] This is a purely arithmetical relation due to the way we calculate mol fractions; thus, the mol fraction of A in B is numerically the same if we consider both to be diatomic or both monatomic, as ½ ÷ (½ + ½) is the same as 1 ÷ (1 + 1).

TABLE 1.—Data on Alloys[a]

Alloy No.	°C.	Temp. Recip., $\frac{10^6}{T}$	Molal Concentration, Bi					Molal Concentration, Sb				
			Liquid State, $(x_L')_{Bi}$	Solid State, $(x_s')_{Bi}$	Ratio, $\left(\frac{x_L'}{x_s'}\right)_{Bi}$	Log. of Ratio, $\log\left(\frac{x_L'}{x_s'}\right)_{Bi}$	Heat of Fusion, (cal. per g.), Calc., λ_{Bi}	Liquid State, $(x_L')_{Sb}$	Solid State, $(x_s')_{Sb}$	Ratio,[b] $\left(\frac{x_s'}{x_L'}\right)_{Sb}$	Log. of Ratio, $\log\left(\frac{x_s'}{x_L'}\right)_{Sb}$	Heat of Fusion, (cal. per g.), Calc., λ_{Sb}
1	612	1.130	6.2	0.7	8.860	0.9474	29.3	93.8	99.3	1.058	0.0245	38.4
2	593	1.155	12.5	1.5	8.330	0.9206	29.6	87.5	98.5	1.126	0.0514	40.2
3	570	1.187	19.8	2.5	7.920	0.8987	30.2	80.2	97.5	1.216	0.0849	39.5
4	545	1.223	27.7	4.0	6.925	0.8403	30.0	72.3	96.0	1.329	0.1235	40.2
5	517	1.266	36.5	6.2	5.890	0.7701	29.5	63.5	93.8	1.477	0.1694	40.8
6	484	1.321	46.3	9.2	5.030	0.7016	29.7	53.7	90.8	1.692	0.2284	40.4
7	446	1.391	57.3	13.1	4.375	0.6410	31.4	42.7	86.9	2.035	0.3107	41.6
8	398	1.490	69.7	20.8	3.350	0.5250	33.0	30.3	79.2	2.614	0.4173	41.0
9	341	1.629	84.6	36.1	2.343	0.3698	38.8	15.4	63.9	4.150	0.6181	44.5
10	319	1.690	89.4	45.5	1.962	0.2927	43.4	10.6	54.5	5.145	0.7114	45.8
11	298	1.751	94.1	58.2	1.616	0.2084	52.6	5.9	41.8	7.095	0.8510	49.7
12	285	1.793	97.2	70.0	1.398	0.1455	71.0	2.8	30.0	10.710	1.0278	56.3
13	279	1.812	98.3	78.5	1.250	0.0969	81.7	1.7	21.5	12.640	1.1018	59.1

[a] A critical analysis of the degree of error in the figures given in this table should be made in conjunction with Fig. 1. The figures for the first eight alloys are fairly reliable, while the figures for the rest of the alloys are not so trustworthy.

[b] Because molal concentration in solid state is more than in liquid state for any temperature, the ratios of molal concentrations shown in column 11 have been reversed. Note subscripts.

TABLE 2.—*Data on Alloys*

| Alloy No. | Molal Concentration, Sb | | | | In terms of Bi, $(x_s'')_{Bi} = 100 - (x_s')_{Sb}$ | Molal Conc. of Bi, $(x_L')_{Bi}$ | Log of Mola Ratios, $\log\left(\frac{x_L'}{x_s''}\right)_{Bi}$ |
	Log of Ratio,[a] $\log\left(\frac{x_s'}{x_L'}\right)_{Sb}$	Ratio, [a] $\left(\frac{x_s'}{x_L'}\right)_{Sb}$	Liquid State, $(x_L')_{Sb}$	Solid State $(x_s')_{Sb}$			
9	0.567	3.685	15.4	56.7	43.3	84.6	0.292
10	0.630	4.260	10.6	45.2	54.8	89.4	0.212
11	0.696	4.955	5.9	29.3	70.7	94.1	0.125
12	0.743	5.525	2.8	15.5	84.5	97.2	0.061
13	0.764	5.800	1.7	9.9	90.1	98.4	·0.039

· [a] Figures shown in second column are obtained by projecting horizontally (that is, isothermally) actually observed values as shown in Fig. 2. In other words, had the system continued to obey the laws of ideal solutions, the logarithm of the molal ratios of alloys 9 to 13 would have values shown in column 2. Knowing the mol. ratios (3d column) and the corresponding $(x_L')_{Sb}$ values (4th column), the $(x_s')_{Sb}$ values shown in 5th column are easily obtained. Since these values are expressed in terms of molal concentration of Sb, 6th column includes the molal concentrations in terms of Bi. From Table 1 we obtain molal concentrations of Bi in the melt (column 7), from which we calculate the logarithms of molal ratios (last column).

TABLE 3.—*Data on Alloys*[a]

| Alloy No. | Molal Concentration, Bi | | | | |
	Liquid State,[b] $(x_L')_{Bi}$	Solid State,[b] $(x_s')_{Bi}$	Equiv. Conc. Bi₂, $(x_s'')_{Bi}$	Log. Recalc., $\log\left(\frac{x_L'}{x_s''}\right)_{Bi}$	Log. from Table 2, [b] $\log\left(\frac{x_L'}{x_s''}\right)_{Bi}$
9	84.6	36.1	46.2	0.264	.292
10	89.4	45.5	55.5	0.207	0.212
11	94.1	58.2	67.5	0.144	0.125
12	97.2	70.0	77.8	0.098	0.061
13	98.4	78.5	84.5	0.066	0.039

[a] Plotting these figures in Fig. 2, we note that the figures in Table 2 more probably represent equilibrium conditions. Hence we need to correct the values·in column 3 of this table.

[b] Assuming that Bi₂ exists within this range, equivalent molal concentrations of Bi₂ are calculated (column 4), and logarithms (column 5) are recalculated on the new basis. These are included here for comparison.

Since there is some evidence that bismuth also forms triatomic molecules, as indicated from its vapor densities at high temperatures, the molal concentrations of Bi₃ in alloys 10 to 13 are converted to their corresponding equivalent molal concentrations of Bi₂ as shown in Table 3. Comparing these values with those shown in Table 2, we note that they do not quite agree, even allowing for error due to the difficulty of

approximating the mol concentration in the solidus. However, we have a simple method of ascertaining which set of values represents equilibrium conditions and whether we are fully justified in assuming the formation[8] of Bi_3. Note that the log $(x_L'/x_S')T_{.}^{-1}$ line for Bi (No. 2 in Fig. 2), while fairly straight, does not pass through the point of origin, the melting point of bismuth. Plotting the two sets of derived values in Fig. 2, it
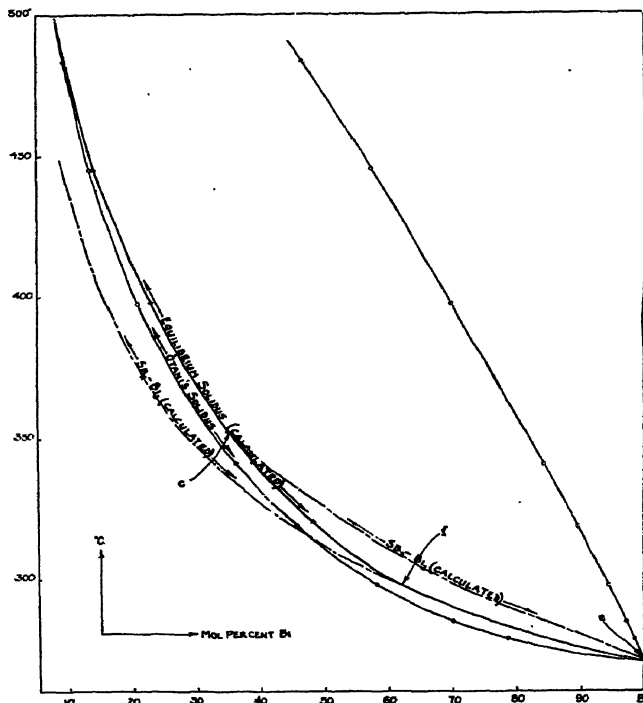
FIG. 4.—PART OF FIG. 3 REDRAWN ON LARGER SCALE.

Note relations of different solidus curves. Based on true ideality of solutions of bismuth in antimony, as inferred from log $(x_S'/x_L')T^{-1}$ curve in Fig. 2, equilibrium solidus is calculated. At c, Bi_3 begins to be stable, so that in range of c-f there is a mixture of Bi_2 and Bi_3 in solid solution with Sb_2. From f to e, equilibrium solidus merges with calculated Sb_2-Bi_3 curve.

is apparent at once from line 3 that the values shown in Table 2 actually represent the equilibrium conditions. Accordingly, from line 3 we can obtain values with which we are enabled to plot the equilibrium solidus as shown in Fig. 4. Ôtani's solidus departs from the calculated equi-

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[8] Assuming that the log (x_L'/x_S') values of the first seven alloys (Nos. 1-7) to be correct as their molal concentrations can be more accurately obtained from Fig. 1, we know that the log $(x_L'/x_S')T^{-1}$ line passing through these points must have a slope which will pass through the point of origin, the melting point of bismuth. Thus, conversely, we can determine the value of n in Bi_n, which is 3.

librium solidus only slightly at high temperatures, but appreciably at lower temperatures. Incidentally, it may be mentioned that the heat of fusion of antimony is not numerically affected by the correction of the Ôtani solidus.

It is important to note in Fig. 3 the alloy which finally solidifies at d has a corresponding point b in the liquidus and another point a in the solidus when solidification begins. Note also that at a the two observed solidi begin to deviate from each other and d marks the beginning of the temperature horizontal in Cook's solidus. Lastly, we see that c—the point defined by temperature and concentration at which Bi₃ begins to be stable —is probably located at around 35 (± 2) mol per cent. Bi, as is d. We cannot, therefore, avoid the conclusion *that in all alloys from composition d (c) to pure Bi, the third phase (solid), that causes the system to behave as if it were under nonvariant equilibrium condition, must be Bi₃.* Thermodynamic reasoning does not, however, enable us to determine whether or not (1) Bi₃ can directly crystallize out of the melt or (2) Bi₃ results from a peritectic reaction of solid solution α(Sb$_x$-Bi₂) with the melt according to the equation

$$\alpha(\text{Sb}_x\text{-Bi}_2) + \text{Melt} \rightleftharpoons \beta(\text{Sb}_x\text{-Bi}_3) \qquad [2]$$

in which α and β are indistinguishable from each other microscopically (Fig. 5). The writer believes the latter to be more probable because the liquidus shows no break or marked deviation from the normal path. It is quite probable that upon prolonged anneal the peritectic reaction may be suppressed upon heating up again, so that the reaction may be considered irreversible. The writer plans to work on this problem in the near future, by means of X-ray crystal analysis.

ATOMICITY OF ANTIMONY AND BISMUTH FROM THEIR HEATS OF FUSION

Many authorities do not agree as to the atomicity of bismuth and antimony. For example, Johnsen[9] found Bi₂ vapor at 1600° to 1700° C. and Biltz and von Meyer found the vapor density to correspond to both Bi₂ and Bi₃, mostly Bi₂. The latter also found this variation, to some extent, in the case of antimony vapor. Heycock and Neville found bismuth and antimony to be monatomic when using cadmium and tin as the solute for the determination of the lowering in freezing point, but using lead as a solvent, they found both bismuth and antimony to be diatomic. This can be explained easily by the fact that the Raoult-van't Hoff law

$$-\Delta t_F = \frac{RT^2_F}{L_{F_0}} x' = kx' \qquad [3]$$

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[9] Most of the physical data introduced here are merely to corroborate what we have already learned from a thermodynamic analysis; hence, it should be sufficient to quote from Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry. 9, 364 *et seq.*; 604 *et seq.* New York, 1929. Longmans, Green and Co.

(in which basically the depression in the freezing point, Δt_F, is directly proportional to the mol concentration of the solute, x') no longer applies to systems showing an appreciable solid solubility. Bismuth and antimony are not appreciably soluble in the cadmium and tin, which crystallize from the melt, but they form limited solid solutions with lead, in which case only the following equation, which is an extension of the Raoult-van't Hoff law, is applicable, thus

$$-\Delta t_F = \frac{RT^2_{F_o}}{L_{F_o}}(x_L' - x_S') = k(x_L' - x_S') \qquad [4]$$

The depression in the freezing point is now proportional to the difference between the molal concentrations of the solute distributed in the liquid and solid phases. Hence, we are not certain that Heycock and Neville's conclusion regarding the atomicity of bismuth and antimony in lead alloys is valid. (The writer discusses this point at some length because an indiscriminate use of the Raoult-van't Hoff law leads only to confusion.)

A. Jouniaux, from Trouton's rule and from observations on antimony amalgams, concluded that antimony is monatomic. W. Herz, and Awberry and Griffiths, give the heat of fusion of antimony as 24.2 and 24.3 cal. per gram respectively, indicating that they consider antimony to be diatomic, since the generally accepted value is around 40 cal. per gram. Richards, too, gives the heat of fusion of antimony as 16 to 27.25 cal. per gram.

Antimony is known to have a monotropic form known as "explosive," which according to Wulff, is amorphous. The heat of transformation with diminution in volume (that is, increase in density from 5.78 to 6.52) is, strangely enough, about 20 cal. per gram. Unfortunately, no X-ray data are available of the structure of antimony after the monotropic transformation has taken place. Whatever may be the cause of the formation of amorphous antimony, we can interpret the transformation as monatomic crystallization from a highly supercooled liquid with the corresponding evolution of heat of crystallization, 20 cal. per gram. A transformation from a monatomic crystalline form to the normal stable diatomic configuration should also give 20 cal. per gram as the heat of reaction.

The ratio of electrical conductivity of metals in the liquid and solid states is about 1:2, but Tsutsumi[10] finds that antimony and bismuth have a ratio of about 1.49 and 2.32 instead of 0.50. *According to him, the abnormality is probably due to a transformation in the molecules during the process of fusion of these metals.* Moreover, we know that they expand upon solidification to the extent of 0.95 and 3.30 per cent. respectively. The abnormally high resistance in the solid state, together with

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[10] H. Tsutsumi: On the Variation of Electric Resistance during the Fusion of Metals. *Sci. Repts.*, Tôhoku Imp. Univ. (1918) **7**, 93.

their positive coefficient of expansion on solidifying, indicates the existence of compounds, or molecular groupings.

In the course of his studies on the theoretical interpretation of the heats of fusion, the writer observed that if we plot the heat of fusion of the elements against their atomic weights, we find the usual periodicity of values.[11] To preserve the periodicity, the heat of fusion of antimony should be only 20 cal. per gram.

The writer has examined the X-ray diffraction patterns of both antimony and bismuth and found them to be identical except for the
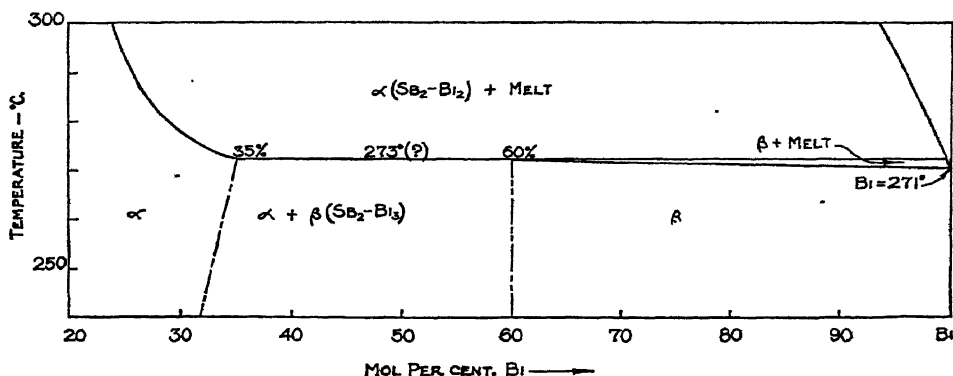
FIG. 5.—PROBABLE PERITECTIC REACTION IN SYSTEM ANTIMONY-BISMUTH.

Existence of two series of solid solutions is postulated. Solid solution α is normal solid solution of Sb_2-Bi_2, while solid solution β results from peritectic reaction due to formation of Bi_3. Peritectic temperature is also postulated as close to real melting point of bismuth as shown in diagram.

larger lattice parameter of the latter. It is outside the scope of this paper to discuss the crystallography of these metals; we shall confine our discussion to the descriptive features of their structure. A. Johnsen found the evidence obtained from X-ray patterns of bismuth to be consistent with the assumption that the molecule is diatomic, and since there is no difference in the structure of bismuth and antimony, we are left with the inference that antimony must also be considered diatomic. Both crystallize in the triangular (hexagonal) system, which may be thought of as being built up of three interpenetrating simple triangular lattices. From another point of view, the structure may be considered to be built of two interpenetrating face-centered rhombohedrons (that is, distorted cubes). It is quite conceivable, from such a picture of the more complicated structure of these two metals, that there exist molecular groupings of two or three, as inferred from thermodynamic data. We know that arsenic and black phosphorus have the same structure as

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[11] To be published later.

antimony and bismuth, and it is, therefore, interesting to note that in the vapor state of arsenic even tetratomic molecules are found.

Turning now to the heat of fusion of antimony and bismuth, we note from equation 1 that solving simultaneously two equations at different temperatures will give the slope of the log $(x_L'/x_S')T^{-1}$ line, which is the heat of fusion of the metal concerned. Strictly speaking, the log $(x_L'/x_S')T^{-1}$ line cannot be perfectly straight because the specific heats of the metals in the solid and liquid states change with the temperature. Nevertheless, we obtain roughly the heat of fusion of antimony and bismuth as 40.7 and 31.2 cal. per gram, respectively. A more reliable method (from a mathematical standpoint) of obtaining the heat of fusion of
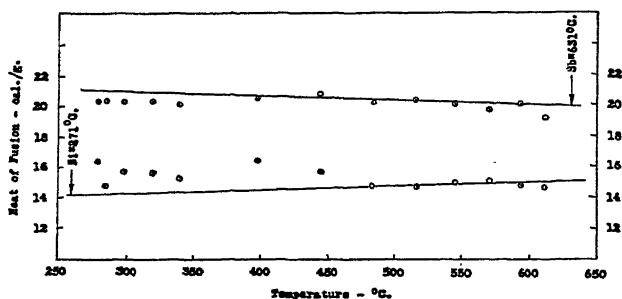
FIG. 6.—HEAT OF FUSION OF ANTIMONY AND BISMUTH.
Mean heats of solution (fusion) of different alloys included in Table 1 are shown, plotted against their respective temperatures. By extrapolation to melting points, true heat of fusion is obtained for both antimony and bismuth.

metals at their melting points is to calculate by the use of equation 1 the *mean heat of fusion* between the melting point and the temperatures shown in Table 1. Such a method defines the true heat of fusion for these reasons:[12] what we really obtain is a series of mean values of the heat of fusion between T_{F_0} and T', so that as T' approaches T_{F_0}, L_F (mean) approaches L_{F_0}. (We do not, therefore, need to know the actual values of the change in the specific heats involved with respect to temperature.) Hence, if we plot the calculated heats of fusion at the different temperatures T', we should obtain by extrapolation the real heat of fusion (L_{F_0}) of the metals at their melting points.

In Fig. 6 the heats of fusion of the first eight alloys in Table 1 and the corrected heats of fusion of alloys 9–13 (Table 2) are shown. Let us first determine which figures are reliable before we draw the curves. In the case of antimony, from Table 1 we know that the data for the first eight alloys are fairly reliable. The corrected heats of fusion (from Table 2)

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[12] A more rigorous mathematical proof may be derived from the exact equations governing the depression of freezing point. Consult the paper referred to in footnote 1.

are also fairly reliable because the log (x'_S/x'_L) values read off from the straight line 1 in Fig. 2 are large enough to minimize the degree of probable error to ± 0.5 cal. per gram. For bismuth, the data for the first six alloys are also reliable. The data for alloys 9 to 13 are susceptible to very large errors in computation—as much as ± 1.5 cal. per gram—because we are dealing with very small log (x'_L/x'_S) values and equally small temperature differences. Hence, we shall disregard these values. The data for alloys 7 and 8 are uncorrected because we do not know the activity-coefficient of (Bi_3/Bi_2). For these reasons, in drawing the heat of fusion curves for bismuth, we shall take into consideration only the first six figures.

Thus we obtain 20 cal. per gram and 14.2 cal. per gram as the heats of fusion of antimony and bismuth respectively, assuming antimony to be diatomic like bismuth. Note, in Fig. 6, that the change in the heat of fusion of the metals is consistent with their known specific heats; that is, since the specific heat of liquid antimony and bismuth is larger than their specific heat in the solid state, the curve for the heat of fusion of antimony with respect to temperature would be expected to have a negative slope and the curve for bismuth, a positive slope.

In Table 4 are shown the values obtained by different workers. It appears that the writer's value for the heat of fusion of bismuth is slightly higher than the majority of values in Table 4, although the heat of fusion of antimony is in good agreement with others. Umino's[13] figures, which may be considered the most reliable, agree very well with the writer's. It may be mentioned here that Umino determined the heats of fusion by comparing the total heat contents of the melt and the solid at the melting point in a vacuum calorimeter. This method of determination is the most accurate one. The method used by Honda and Ishigaki[14] in measuring the depression in freezing point by the addition of 1 to 3 mol per cent. solute is another form of direct determination, but the assumption that the liquidus and solidus are straight in calculating the heat of fusion by equation 4 is open to grave doubts. Almost all the systems they studied possess a concave (curved downward) solidus.

SUMMARY OF PART I

1. The writer has discussed the constitutional diagram of the Sb–Bi system, which for a long time has shown the anomaly of isothermal crystallization of alloys of varying composition. Ôtani redetermined the solidus and found it to be typical of completely isomorphous systems. Yet we always obtain the Cook solidus from thermal cooling curves.

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[13] S. Umino: On the Latent Heat of Fusion of Several Metals and Their Specific Heats at High Temperatures. *Sci. Repts.* Tôhoku Imp. Univ. (1926) **15**, 597.

[14] K. Honda and T. Ishigaki: On the Law of Depression Point in Metallic Alloys. *Ibid.* (1925) **14**, 219.

No explanation has ever been advanced to account satisfactorily for the temperature horizontal. Microscopic evidence does not reveal the presence of two phases, if two phases do exist. It is possible that eventually an etchant will be found that may reveal some difference in the solid solutions containing up to 35 mol per cent. Bi and the solid solutions containing more than 35 mol per cent. Bi. The most convenient method of studying this problem would be by means of the X-ray crystal analysis.

TABLE 4.—*Heats of Fusion*

Workers	λ(cal. per g.)	λ(cal. per. g.)
Wust and coworkers........................	38.9	10.23
Honda and Ishigaki........................	39.5	10.2
Umino...................................	40.75	14.1
Intl. Crit. Tables (2, 458).................	39.5	17.8
Awbery and Griffiths......................	24.3	13.0
Herz....................................	24.2	12.2
C. C. Person.............................		12.6
Robertson................................		12.64
Mezotto.................................		13.0
Johnston.................................		13.0
Adams...................................		13.0
Yap.....................................	(40.0) 20.0	14.2

2. The thermodynamic laws of solution have been applied to the system in order to investigate the nature of its inner equilibrium and to gain an insight, if possible, into the processes occurring within the solution that result in the anomalous isothermal crystallization. From the evidence thus derived, it seems probable that bismuth also forms Bi_3.

3. Thermodynamics cannot tell us whether solid solution β (Sb_2-Bi_3) is formed directly in the melt due to the direct dissolution of Bi_3 in Sb_2 or, as seems more likely, is the result of a peritectic reaction of solid solution α (Sb_2-Bi_2) with the melt. Annealing for a long time below the melting point of bismuth tends to homogenize completely solid solution β so that upon heating up the peritectic reaction may no longer be reversible.

4. Solid solutions α and β are indistinguishable from each other by ordinary chemical reagents, but it should be possible to detect some slight difference in their internal structure by means of X-ray crystal analysis.

5. Corroborative evidence is introduced incidentally to show that many different investigators have concluded that bismuth and antimony are diatomic and that they also form, to some degree, triatomic molecules. It is precisely this tendency to form triatomic molecules that causes the observed isothermal crystallization.

6. The heats of fusion of bismuth and antimony have been calculated to be 14.2 and 20 cal. per gram, which are in good agreement with recent experimental results (e. g., Umino's).

7. It is surprising to observe how well such an abnormal system as the Sb-Bi system obeys the thermodynamic laws of ideal solutions. For the benefit of those who may not be fully familiar with the method adopted in this paper, the writer has included a rather elaborate and intensive analysis of the derived thermodynamic data. He hopes to have shown that the thermodynamic method is capable of yielding considerable information not obtainable otherwise by ordinary physical metallurgical methods of investigation.

PART II.—LEAD-RICH END OF ANTIMONY-LEAD SYSTEM

In order to avoid unduly lengthening this paper, we shall deal only with the lead end of the antimony-lead system, because of its great practical importance as lead sheath for cables. The liquidus and the solidus of the system, as well as the solid solubility of antimony in lead, have been determined by Dean,[15] Schumacher[16] and their associates. It may safely be said that their experimental results represent a high degree of accuracy. The writer is interested in investigating the lead-rich end of the system from a thermodynamic point of view. It is unfortunate in a sense that the solute happens to be antimony, which like bismuth, behaves abnormally in many ways. The writer is pleased, however, to discover, as will be shown below, that the behavior of antimony in the lead-antimony system is consistent with the theory advanced in Part I that both antimony and bismuth should be considered normally diatomic, so that the heat of fusion of the former should be 20.0 cal. per gram instead of the generally accepted value of 40 cal. per gram.

The liquidus of the lead-rich end of the antimony-lead system is almost a straight line, slightly curving downward, as shown in Fig. 7, although a convex liquidus might be expected, on account of the convex solidus. This indicates strongly that the identity of the reactants in the melt is not the same as of those in the solid, as was found in the iron-carbon system. As the tendency to undercooling is well known in these alloys, the degree of

[15] R. S. Dean: The Lead-Antimony System. *Jnl.* Amer. Chem. Soc. (1923) **45,** 1683.

R. S. Dean, L. Zickrick and F. C. Nix: The Lead-antimony System and Hardening of Lead Alloys. *Trans.* A. I. M. E. (1926) **73,** 505.

[16] E. E. Schumacher and F. C. Nix: The Solidus Line in the Lead-antimony System. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 195.

E. E. Schumacher and G. M. Bouton: The Solid Solubility of Antimony in Lead as Determined by Conductivity Measurements on Cold-Worked Alloys. *Jnl.* Amer. Chem. Soc. (1927) **49,** 1667.

accuracy of the thermal data obtained by Dean in determining the liquidus[17] is not comparable to the degree of accuracy of the solidus determined by the Heycock and Neville method.[18] A vertical displacement of only 2° C. produces as much as 0.5 per cent. displacement in the concentration of the liquidus on account of its slope. Since there is a fair agreement of the thermal data, we shall accept the curved liquidus
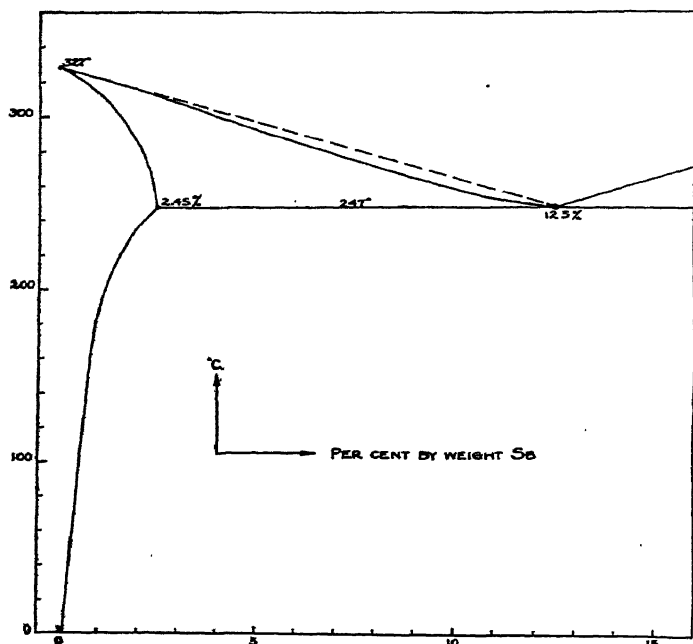
FIG. 7.—CONSTITUTIONAL DIAGRAM OF SYSTEM ANTIMONY-LEAD. (AFTER DEAN, SCHUMACHER AND ASSOCIATES.)

as correct and then compare the results of our calculations with others made on the basis of an ideal straight liquidus. It must be pointed out here that when we convert the diagram (Fig. 7) to mol per cent. Bi (which has been determined to be the correct identity of the solute in molten lead) the deviation from a straight line is much less. Hence, we might reasonably attribute the slight deviation from the ideal liquidus to the incomplete dissociation of Sb_2 to Sb in molten lead.

SOLID SOLUBILITY OF ANTIMONY IN LEAD

Although antimony is practically insoluble in lead at room temperature, at 247° C. it is soluble up to about 2.45 per cent. by weight. Fig. 8

[17] Reference of footnote 15.
[18] Reference of footnote 16.

shows the solid solubility curve of antimony in lead. Only seven points on the curve have been determined, five being contributed by Schumacher and Bouton and two by Dean. The curve consists essentially of two parts; namely, up to about 150° C. it is practically a straight line, but above that temperature the solubility is no longer a linear function. Note that in $C_0 - C_2$, projected to 247° C., C_2 approximates one-half the value of C_1, the exact half-value being located at C_3. Expressed in mol per cent., C_2 and C_3 are even closer together. The line C_0C_3 is well within the limits of the allowable experimental error, as shown in Fig. 8.
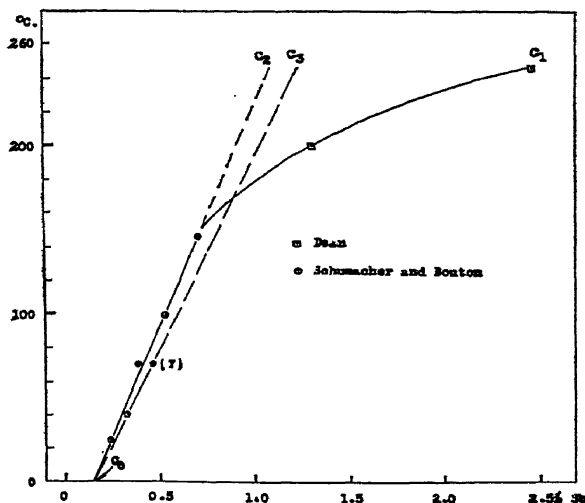
FIG. 8.—SOLUBILITY CURVE OF ANTIMONY IN LEAD. (AFTER DEAN, SCHUMACHER AND BOUTON.)

This strongly suggests a transformation either of antimony or of the solid solution at around 150° C. (probably lower). Below that temperature, antimony is dissolved as monatomic Sb, but above it, the solute is evidently Sb_2. The breakdown of Sb from the diatomic to the monatomic form may be conceived to have been brought about by the extremely severe cold working.[19]

Let us first examine, by calculating the heat of solution of antimony in lead, the atomicity of the solute. The change in solubility in dilute solutions with respect to temperature (absolute) is given by the thermodynamic equation

$$2.3 \log \frac{s'}{s} = \frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) \qquad [5]$$

[19] The lead wires were severely cold-worked first to accelerate the precipitation of the excess antimony and thus bring about equilibrium quickly.

where s' and s are the solubilities of the solute (expressed in any units) at temperatures T' and T, and Q is the molal heat of solution. Taking 0.7 per cent. as s' at 146° C. and 0.24 per cent. as s at 25° C. we obtain by substitution

$$2.3 \log \left(\frac{0.70}{0.24} \right) = \frac{Q}{R} \left(\frac{1}{298} - \frac{1}{419} \right)$$

from which we calculate the heat of solution Q to be about 2180 cal. per mol, or 18.0 cal. per gram of antimony. The writer has shown in Part I that antimony should be considered normally diatomic in the Sb-Bi system and therefore its heat of fusion (equivalent to solution in this case) should be 20 cal. per gram instead of the commonly accepted value of 40 cal. per gram. On the basis of the $C_0 C_3$ line, s' would then be about 0.8 per cent. antimony and the heat of solution recalculated will be found to increase to 20 cal. per gram.

Let us now investigate the curved part of the solubility line in Fig. 8 According to equation 5, if we plot $\log s$ against $(1/T)$ the slope of the locus of the different points should give the heat of solution as before. In Fig. 9 are plotted the three observed points and three points obtained by interpolation from Fig. 8. Note that the scale used is fairly large, so that taking into account the change in the heat of solution due to the change in the heat capacities involved, we are fairly justified in drawing line AB as shown. The slope of the line gives 42 cal. per gram as the heat of solution of antimony in lead, which enables us to conclude that in this range the solute is Sb_2. If we draw line $A'B'$, allowing an error of 9° C. in Dean's value for the 1.3 per cent. antimony alloy, the slope of the line gives 44.7 cal. per gram, which still is within experimentally observed value. However, if we assume the transformation point to be lower than 150° C., the slope naturally decreases and, accordingly, the heat of solution also.

In Fig. 7, part of the antimony solubility line (liquidus) has been carefully determined. Thus, an alloy containing 16 per cent. antimony by weight has a melting point of about 270($\pm$1)° C. and the eutectic contains 12. 5 per cent. antimony. Converting them to mol fractions, we have 0.2450 and 0.1955 respectively. Substituting these values in equation 1 and taking 247° C. as the eutectic temperature, we obtain the heat of solution (that is, fusion in this case) of antimony to be about 21.5 cal. per gram. Therefore, in the range included in Fig. 7, antimony is dissolved in the melt in the monatomic form[20] and we shall accordingly assume this fact as a basis of our subsequent calculations.

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[20] From the shape of the liquidus on the antimony-rich side of the system, we infer antimony to exist there as Sb_2. Unfortunately, the liquidus is not sufficiently investigated to make it worth while to subject the antimony-rich side of the system to a thermodynamic analysis. The dissociation of Sb_2 to Sb in the presence of a considerable amount of Pb atoms in the melt is not unexpected.

It is remarkable, indeed, that the calculated heat of solution, whether in the melt or in solid solution, is, within the limits of allowable error, identical in value. On general thermodynamic grounds, since the antimony has never really crystallized (*i. e.*, built up its own crystal form) we should, therefore, expect its heat of solution (fusion) in the melt to be identical with its heat of solution in the solid lead.[21] If this should hold as a general rule, we have a convenient method of calculating the heat of fusion of metals and compounds possessing high melting points. We have, of course, several empirical rules which give very roughly the magnitude of the heat of fusion.

EQUILIBRIA OF ANTIMONY-LEAD ALLOYS FROM STANDPOINT OF IDEAL SOLUTION

Points were obtained from the original enlarged diagram of Fig. 7 and converted to mol per cent. concentrations of lead (solvent). The
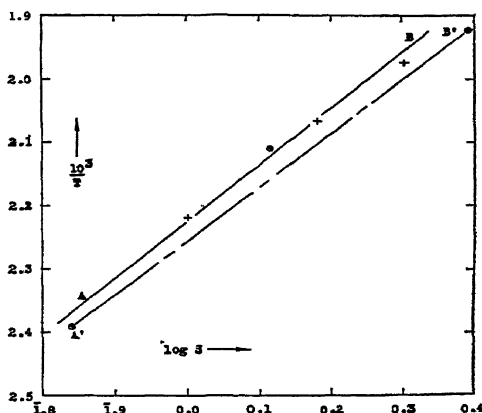
FIG. 9.—PART OF SOLUBILITY CURVE IN FIG. 8 PLOTTED ACCORDING TO EQUATION 5.

data are tabulated in Tables 5 and 6 and plotted as shown in Fig. 10. The scale used is large enough to accentuate, rather than disguise, any deviation from a straight-line function. It is evident in Fig. 10, that, even on the assumption that we have an ideal straight liquidus, curve 2 deviates appreciably from a straight line. However, when antimony is assumed to be diatomic in solid solution in lead, although it dissociates to the monatomic form in the lead-rich melt, the convex of curve 3 is much less. Finally, when the ideal straight liquidus is used as the basis of computation, we have an almost straight line. Hence, we are entirely justified in concluding that *when true (complete) equilibrium is*

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[21] In a paper now in course of preparation, the writer will show that this is also true in the case of Fe_3C.

established in both the liquid and solid phases, antimony is dissolved in the melt in the monatomic form, but is dissolved in the solid solution as diatomic antimony. Just how the antimony molecules are distributed

TABLE 5.—*Different Concentrations of Antimony in Liquid and Solid Phases, Expressed First as Percentage by Weight, Then Converted to Mol Per Cent. Sb and Sb₂*

t °C.	Liquidus			Solidus		
	Sb, Per Cent.	$(x_L')_{Sb}$		Sb, Per Cent.	$(x_S')_{Sb}$	$(x_S')_{Sb_2}$
315	1.70	2.84		0.80	1.35	0.68
300	3.60	5.97		1.50	2.53	1.28
282	6.25	10.18		2.00	3.36	1.71
267	8.40	13.50		2.25	3.77	1.92
247	12.50	19.55		2.45	4.09	2.09

TABLE 6.—*Data for Curves Shown in Fig.* 10

(x_S')	(x_L')	$\log \left(\dfrac{x_S'}{x_L'} \right)$	t °C.	T'	$\dfrac{10^3}{T'}$
1. DATA FOR CURVE 1					
0.9865	0.9716	0.00–762	315	588	1.7007
0.9746	0.9403	0.01–560	300	573	1.7452
0.9664	0.8982	0.03–179	282	555	1.8018
0.9623	0.8650	0.04–629	267	539	1.8553
0.9591	0.8045	0.07–633	247	520	1.9231
2. DATA FOR CURVE 2					
0.9865	0.9690	0.00–778	315	588	1.7007
0.9746	0.9325	0.01–922	300	573	1.7452
0.9664	0.8880	0.03–675	282	555	1.8018
0.9591	0.8525	0.05–262	267	539	1.8553
3. DATA FOR CURVE 3					
0.9932	0.9716	0.00–955	315	588	1.7007
0.9872	0.9403	0.02–114	300	573	1.7452
0.9829	0.8982	0.03–914	282	555	1.8018
0.9808	0.8650	0.05–456	267	539	1.8553
0.9791	0.8045	0.08–530	247	520	1.9231
4. DATA FOR CURVE 4					
0.9932	0.9690	0.01–072	315	588	1.7007
0.9872	0.9325	0.02–476	300	573	1.7452
0.9829	0.8880	0.04–410	282	555	1.8018
0.9808	0.8525	0.06–089	267	539	1.8553

in the space lattice of the solvent (lead) is beyond the scope of this paper, as no X-ray data on the subject are available to the writer as a basis for discussion.

It will confirm our conclusions if we can obtain a value of the heat of fusion which agrees with the observed values. We cannot use equation 1 because in deriving it we did not take into account any dissociation or association of one of the components in the course of a change of state (i. e., solidification). It can be easily shown by thermodynamics that the
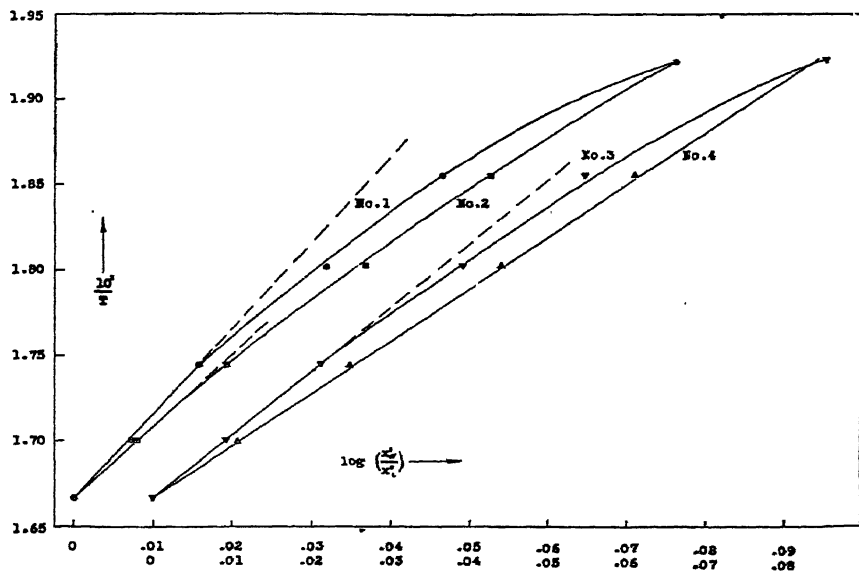
FIG. 10.—LOG $(x_S'/x_L')T^{-1}$ CURVES PLOTTED FROM DATA IN TABLES 1 AND 2.

Curve 1.—Antimony calculated as monatomic in both liquid and solid states.
Curve 2.—Same as curve 1, except that ideal straight liquidus is assumed to be correct.
Curve 3.—Antimony calculated as dissolved in solid solution as diatomic.
Curve 4.—Same as curve 3, except that ideal straight liquidus is assumed to be correct.

following equation holds when a diatomic solute dissociates to the monatomic form upon melting:

$$\log\left(\frac{x_S'}{x_L'}\right) - 2\log\left(\frac{x_S'}{x_S''}\right) = \frac{L_{F_e}}{2.3R}\left(\frac{1}{T_{F_e}} - \frac{1}{T'}\right)$$

in which [2 log (x_S'/x_S'')] takes care of the additional heat due to the dissociation of the solute, x'' being the equivalent molal concentration of the solvent in which the solute is assumed to be completely dissociated to the monatomic form. Substituting all the necessary values, we have

$$\log\left(\frac{0.9791}{0.8045}\right) - 2\log\left(\frac{0.9791}{0.9591}\right) = \frac{L_{F_e}}{2.3R}\left(\frac{1}{600} - \frac{1}{520}\right)$$

which, solving for L_{F_o} and dividing by 207.2, gives 5.7 cal. per gram as the heat of fusion of lead, in good agreement with the experimentally derived values of 5.3 to 6.4 cal. per gram.[22]   Umino's value,[23] which may be considered the most reliable, is 5.5 cal. per gram.

SUMMARY OF PART II

1. Attention is called to the probability of a transformation either of antimony or of the lead solid solution at around 150° C.   Below the transition temperature, antimony is dissolved as Sb, but above the transition temperature up to the melting point of pure lead, the solute is Sb_2.

2. The heat of solution of antimony is calculated to be about 18 cal. per gram.   A slight change (well within the allowable limits of experimental error) in the slope of the solubility line (that is, the straight part) will easily increase the heat solution to 20 cal. per gram, which is identical with its heat of fusion.   The heat of solution of Sb_2 in lead (above 150° C.) is also calculated to be about 42 cal. per gram.

3. It is concluded that since antimony has never solidified in the sense that it has built up its own crystal form, the heat of solution in the solid state is identical in nature with the heat of solution (fusion) in the melt.   This relationship, if well established in the future, will prove very useful in allowing us to calculate the heat of fusion of metals and compounds, otherwise difficult to calculate or determine experimentally. .

4. The lead end of the antimony-lead system has been subjected to a thermodynamic analysis from the standpoint of the laws of ideal solution. It is found that on the assumption that the observed liquidus is slightly incorrect, the conclusion that antimony exists as monatomic antimony in the melt, but is dissolved in solid solution in the diatomic form, is entirely consistent with the observed behavior of the system as deduced from a thermodynamic analysis.

5. The heat of fusion of lead is calculated to be about 5.7 cal. per gram, which is in good agreement with values obtained experimentally.

ACKNOWLEDGMENT

DISCUSSION

C. BENEDICKS, Stockholm, Sweden (written discussion).—The importance of applying thermodynamic calculations to metallographic systems can scarcely be exaggerated.   On the other hand, a critical scrutiny of the experimental results is even still more necessary.   Before drawing the conclusion that the striking partly horizontal shape of the solidus curve Sb–Bi—as determined by ordinary cooling curves—may

[22] Reference of footnote 14 and Int. Crit. Tables, 2, 458.
[23] S. Umino: Op. cit.

prove that the Bi atoms occur in a triatomic state, connected with a hypothetical peritectic reaction, it is indispensable to ascertain whether the shape of the curve may not be due to experimental difficulties.

A much more natural explanation actually presents itself. The diagram shows that the mixed crystals first formed are very rich in antimony. In order to enable these crystals on cooling to react with the liquid phase, as equilibrium demands, so as to form crystals richer in bismuth, two conditions are necessary: (1) The cooling must be very slow, the diffusion speed in the Sb-Bi alloys being rather low; (2) the antimony-rich mixed crystals must be surrounded by the bismuth-rich liquid alloy, otherwise bismuth cannot be absorbed in the degree corresponding to equilibrium. Now the antimony-rich crystals have a much lower density than the bismuth-rich melt. The consequence will be that the crystals formed have a great tendency to rise to the upper part of the melt, and the adjacent part of the melt will soon be poor in bismuth. Hence a very effective stirring and a very slow cooling are indispensable if equilibrium is to be attained. Otherwise, the liquid finally solidifying will be nearly pure bismuth. The extension of the solidification point of bismuth towards antimony consequently is explained merely by the fact that equilibrium is rather difficult to attain.

This explanation is scarcely a new one, as Hüttner and Tammann in the first paper on the system rightly emphasize both factors concerned.

YAP, C. P. (written discussion).—I am aware of the work of Hüttner and Tammann, and of their explanation. I think Dr. Benedicks will agree with me that often the most plausible explanation may not be the right one, and I believe that it is so in this case. There are two simple reasons against the acceptance of the explanation advanced by Hüttner and Tammann: (1) the solidus is straight from the melting point of antimony to about 35 per cent. Bi, and (2) no variation in the liquidus is observed by the different investigators of the system. The relation between *a–b–c–d* and the Cook solidus is too striking to be accidental, therefore I suggest an explanation based on a peritectic reaction. I have been studying the possibility of explaining a peritectic reaction on the basis of a pseudoternary system; in the present instance, $Sb_7-Bi_7-Bi_3$. The ordinary diagram (that is, with the Cook solidus) is certainly suggestive of a binary cross-section of a ternary diagram.

Cemented Tungsten Carbide; a Study of the Action of the Cementing Material

By L. L. Wyman* and F. C. Kelley,* Schenectady, N. Y.

In order to clarify and amplify the existing data concerning the action of the cementing material in cemented tungsten carbide alloys, the authors have initiated this investigation of the entire range of cobalt-tungsten carbide alloys. Inasmuch as the ultimate objective is relative to what actually goes on during the sintering of cemented tungsten carbide materials, this work was necessarily restricted to heat treatments similar to those used in actual production of these materials. In the course of numerous experiments, the authors have noted several conditions that indicated that there was a solubility to be considered. Among these factors are the following:

1. Many of the alloys showed a much larger amount of binding constituent to be present than could possibly be accounted for by the cobalt content.

2. In many areas, grains of the carbide constituent are much larger than the particles of carbide originally added. In addition, these grains are of very regular contour.

2a. In samples of cemented tungsten carbide which had been fused in the atomic hydrogen torch in the presence of excess binder constituent, immense grains are formed, and their shapes are very regular. This is also true when the cemented tungsten carbide of 13 per cent. Co content is fused alone in the atomic hydrogen torch. Contrary to general expectation, chemical analysis of this material, after fusion in the atomic hydrogen torch, checks the analysis of unfused material.

3. In making the cemented tungsten carbide materials by the process of exerting the pressure at the time of heating a certain portion of the contents squeezed out of the mold. Chemical analysis has shown that this material contains approximately 12 to 20 per cent. of tungsten. The microstructure shows a cored dendritic structure interlaced with eutectic network, and some graphite, as shown in Fig. 1.

4. Thermal analysis of these materials has consistently indicated an arrest point close to 1350° C.

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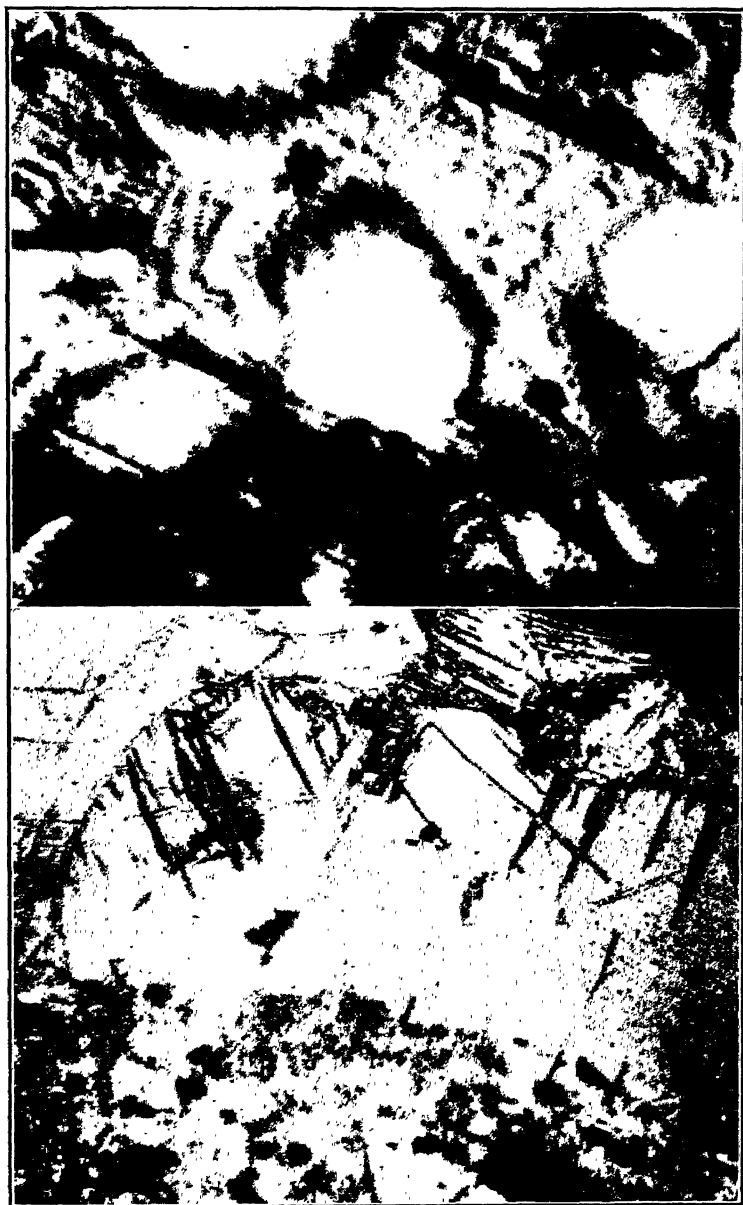
FIG. 1.—Co, 80, WC, 20 PER CENT.   × 1500.
Etched with 50 per cent. nitric acid + 50 per cent. alcohol.
FIG. 2.—PURE Co.   × 200.
Etched with acid ferric chloride.

Considering this arrest point in conjunction with the fact that the lowest temperature required to sinter the cemented tungsten carbide materials is coincidently about 1350° C., a fusion is indicated.

EXPERIMENTAL CONDITIONS

In order to obtain some definite information as to what actually takes place during the manufacture of cemented tungsten carbide materials, the authors decided to investigate microscopically the entire range of these materials; the alloys being subjected to the same heat treatment that is employed in the regular manufacture of these products, namely, sintering for $1\frac{1}{2}$ hr. at 1400° C. The pieces to be sintered were placed on a slab of Al_2O_3, placed in graphite boats, and heated in hydrogen furnaces for the desired time and temperature. The materials used were identical with those used in regular production, all of the alloys being made from the same lots of raw powder materials.

EXPERIMENTAL RESULTS

Two important factors must be recognized in interpreting the results of these experiments:

1. The $1\frac{1}{2}$-hr. treatment at 1400° C. is insufficient to attain equilibrium conditions.

2. The tungsten carbide particles are so much more dense than the cobalt phase that severe segregation takes place in the alloys that melt during the heat treatment.

The pressed bar of pure powdered cobalt, after sintering, showed a very porous and fine-grained core, surrounded by a case approximately 0.020 in. thick, which had been fused, leaving a very large-grained structure (Fig. 2).

Inasmuch as the melting point of pure cobalt is 1480° C., it is evident that the exterior layer of the cobalt has become carbonized, lowering its melting point.

The alloys containing 5 and 10 per cent. WC show the presence of a needlelike second phase and some solution taking place in the grain boundaries (Figs. 3 and 4). No particles of the original carbide could be observed. The alloy containing 15 per cent. WC shows locally the presence of a eutectic formation around the dendritic matrix (Fig. 5). At 20 per cent. WC, the structure shows cored dendrites surrounded by a eutectic network (Fig. 6).

It is interesting to note that the microstructure of this alloy is in close agreement with the structure obtained from the excess squeezed out during the manufacture of cemented tungsten carbide by the hot pressing method, the chemical analyses of which are approximately the same.

At a content of 27.5 per cent. WC, there appears a large amount of eutectic structure, forming the background for the solid solution dendrites.

Fig. 3.—WC, 5, Co, 95 PER CENT.   × 1500.
Fig. 4.—WC, 10, Co, 90 PER CENT.   × 1500.
Both etched with acid ferric chloride.

FIG. 5.—WC, 15, Co, 85 PER CENT.   × 1500.
Etched with acid ferric chloride.
FIG. 6.—WC, 20, Co, 80 PER CENT.   × 1500.
Etched with 50 per cent. nitric acid + 50 per cent. alcohol.
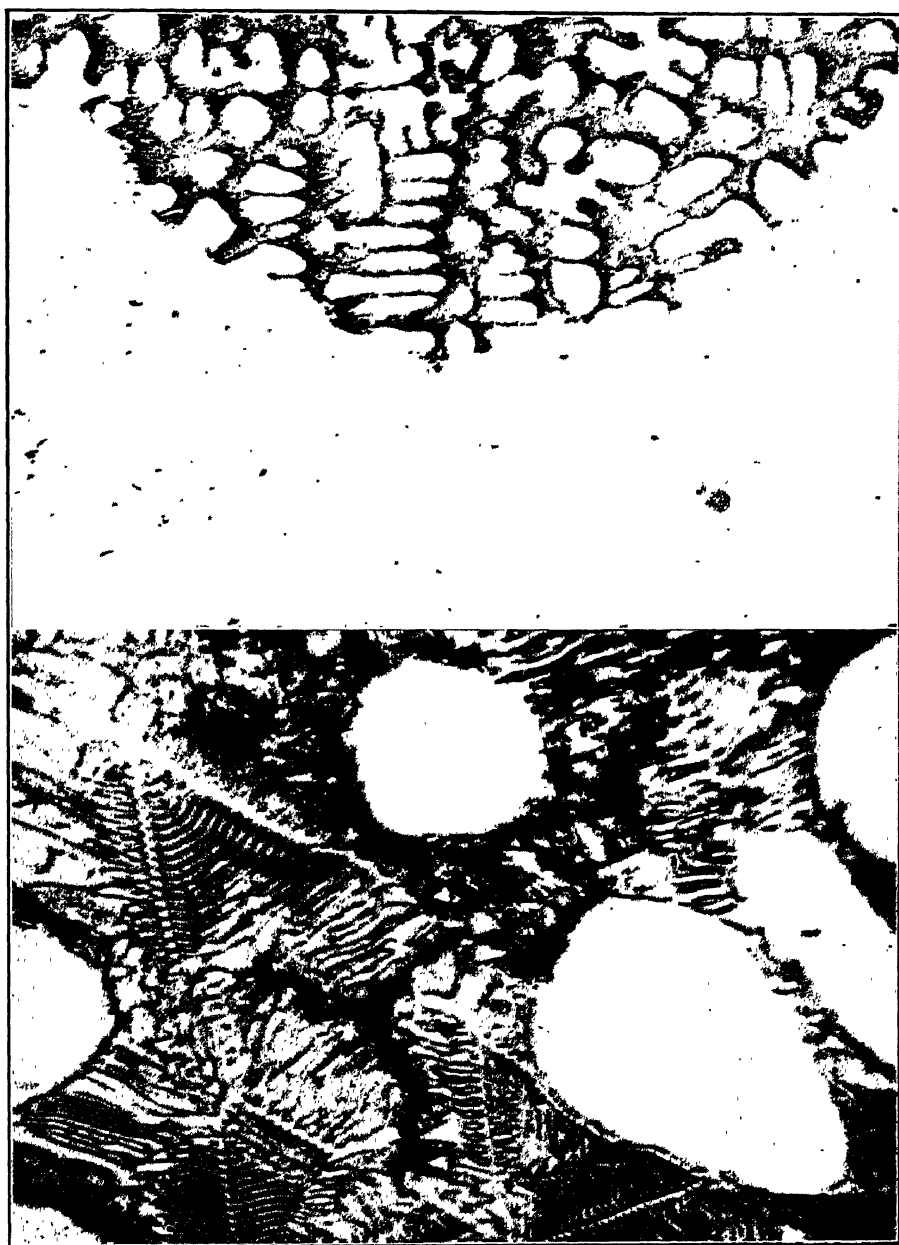
FIG. 7.—WC, 27.5, Co, 72.5 PER CENT.   × 200.
FIG. 8.—WC, 27.5, Co, 72.5 PER CENT.   × 1500.
Both etched with acid ferric chloride.

This eutectic structure has apparently two forms, as shown in Figs. 7 and 8. The structure of the bottom part of Fig. 7, which shows only slight markings, is entirely dendritic, surrounded by a network of white eutectic. The differences are very small and in photographing were practically eliminated.

The phase in relief in the clean herringbone structure can be traced to continue into the mottled structure, giving the impression that the two structures have the same constituents but that the dark, mottled areas have been restricted by the graphite plates present. As in all of the previous samples examined, none of the original tungsten carbide particles can be found to persist. The lower part of Fig. 7 consists almost entirely of the herringbone structure, while the upper part is a mixture of herringbone and mottled. Consequently, at the lower magnification the matrix has a dark appearance.

In the alloys containing 30 per cent. WC, there appears a new structure, of eutectic appearance (Figs. 9 and 10). This is definitely different from the structures previously noted, and can be seen readily on the polished, unetched specimen. Its occurrence is that of a gray eutectic network, consisting of needles and figures shaped like arrowheads, which are apparently quite crystalline, surrounding the dendrites. In the few instances where this structure adjoins the herringbone type of eutectic structure, the configuration of the latter is lost (Fig. 11).

In order to gain additional information regarding this herringbone or pine-tree eutectic structure, two samples, of 32 and 34 per cent. WC, were heated for a period of 20 hr. at 1400° C., slowly cooled to the point of solidification and then quenched. Halves of these samples were reheated and cooled slowly to room temperature. In none of these four samples was there an indication of the white structure. The microconstituents consisted of dendrites, surrounded by the gray, crystalline, needlelike eutectic structure and immense rectangular grains (Figs. 12, 13 and 14).

Under these conditions of treatment, it is only logical to assume that the maximum amount of solution has taken place. It is, therefore, again logical to conclude that the white structure is to be associated with a lower degree of solubility of tungsten and carbon than is the gray needlelike structure, and that it is not a stable structure at 1400° C., nor at room temperature for near-equilibrium samples of these compositions. At this composition, it was noted that the amount of dendritic phase had decreased until the alloys consisted of approximately one-half dendrites and one-half eutectic structures.

With a content of 35 per cent. WC, the white herringbone type of eutectic structure and its graphite variation have disappeared and another new constituent is first in evidence (Figs. 15 and 16). The latter

FIG. 9.—WC, 30, Co, 70 PER CENT.   × 200.
FIG. 10.—WC, 30, Co, 70 PER CENT.   × 1500.
   Both etched with acid ferric chloride.

FIG. 11.—WC, 31, Co, 69 PER CENT.   × 1500.
FIG. 12.—WC, 32, Co, 68 PER CENT.   1300° QUENCH.
Both etched with acid ferric chloride.

is composed of small angular grains, usually triangular or rectangular, or combinations of both.   The contours are generally straight-sided.   These alloys are considerably harder, and these angular particles stand in

FIG. 13.—WC, 32, Co, 68 PER CENT.   × 1500.   1300° QUENCH.
FIG. 14.—WC, 34, Co, 66 PER CENT.   × 1500.   SLOW COOLED.
Both etched with acid ferric chloride.

decided relief on the polished face of the sample.   The grains apparently are not attacked by acid reagents, but respond to etching by reagents customarily used for tungsten carbide materials.

Even though some of these alloys show all of the structures mentioned, on the same sample, it is interesting to note that the white herringbone eutectic structure does not appear in areas where the recently noted grains occur. The solubility seems such that the structure is thrown either to one side or the other of the needlelike eutectic structure.

FIG. 15.—WC, 35, Co, 65 PER CENT. × 200.
FIG. 16.—WC, 35, Co, 65 PER CENT. × 1500.
Both etched with acid ferric chloride.

The alloys containing 40 per cent. WC show many of these grains and a very small amount of the needlelike eutectic structure, in relief on an apparent solid solution matrix. The dendrites have entirely disappeared and only these two harder constituents remain in the matrix; the gray needlelike eutectic structure is in evidence only in one small area, thus leaving mainly the grains and matrix(Fig. 17).

At 45 per cent. WC content, the needlelike eutectic structure has completely disappeared and there are only two constituents present:
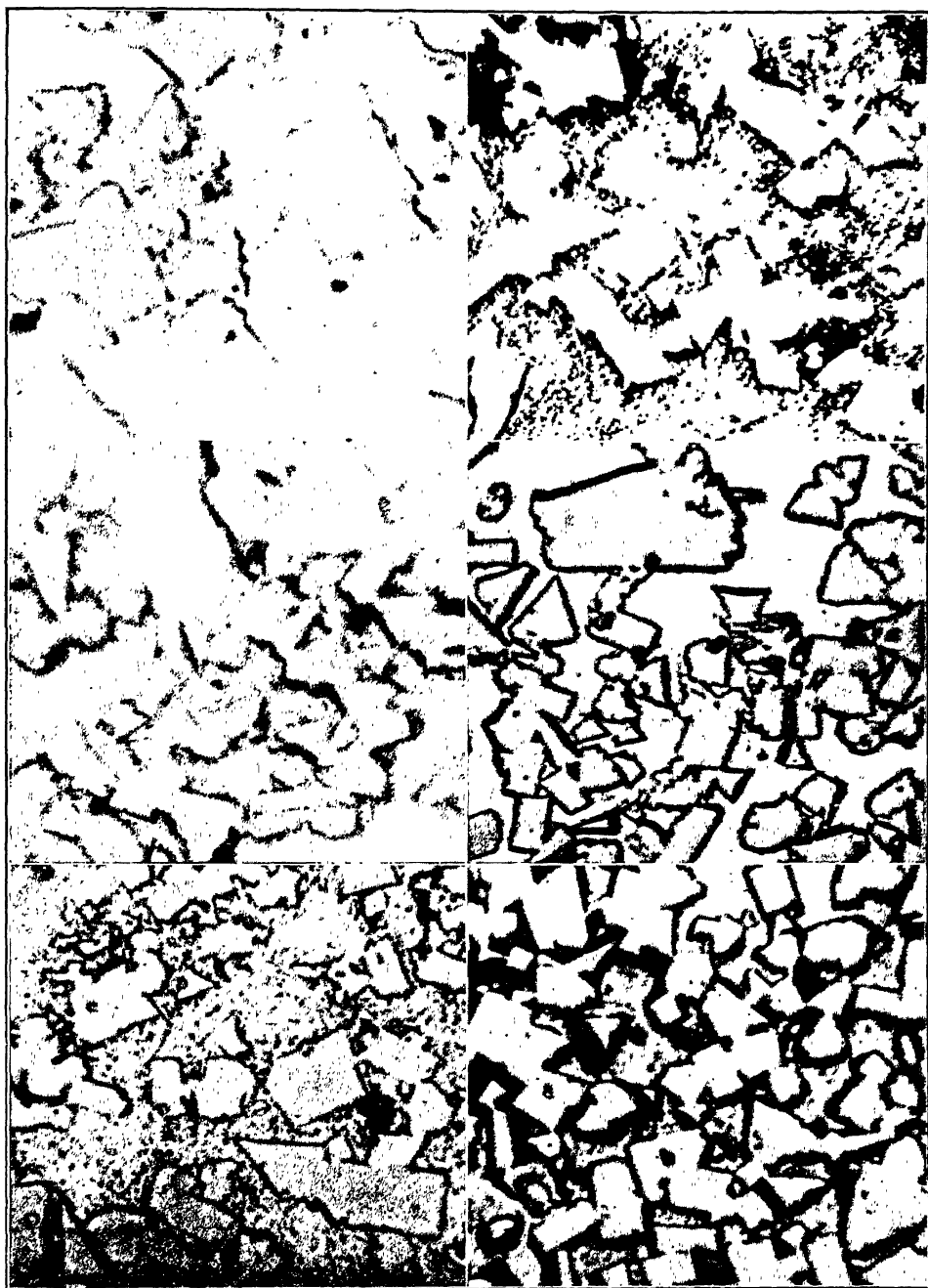
FIGS. 17-22.—CAPTIONS ON OPPOSITE PAGE.

the angular grains in the uniform matrix (Fig. 18). Neither acid nor caustic etchants reveal any complexity in the matrix material.
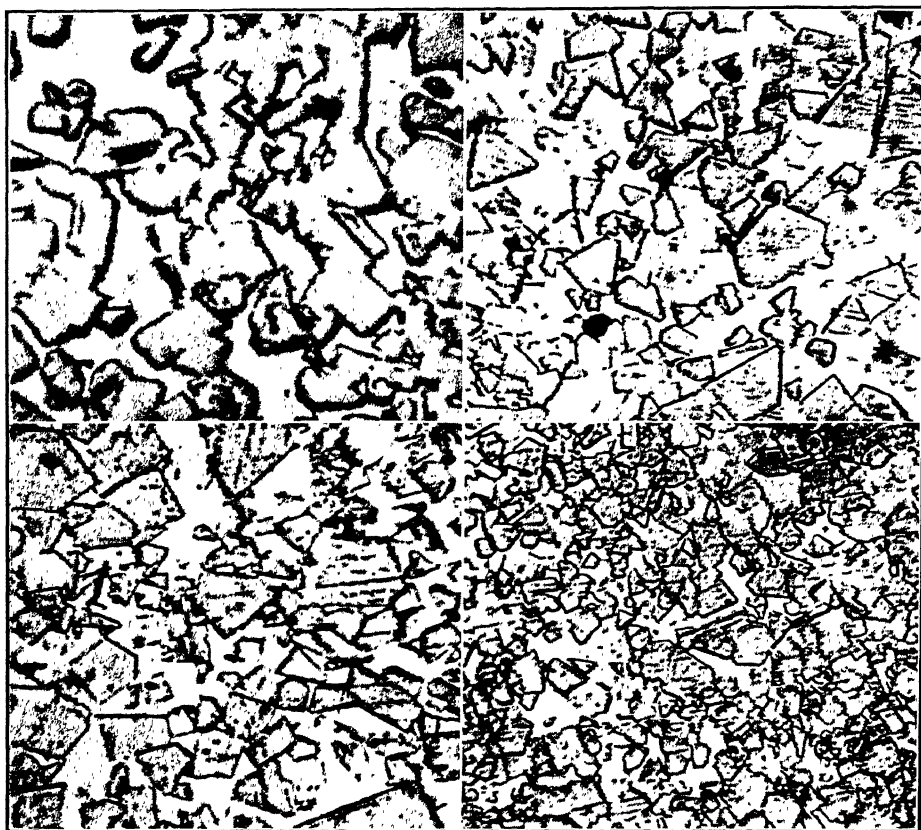
FIG. 23.—WC, 70, Co, 30 PER CENT. × 1500.
Etched with acid ferric chloride.
FIG. 24.—WC, 75, Co, 25 PER CENT. × 1500.
FIG. 25.—WC, 80, Co, 20 PER CENT. × 1500.
FIG. 26.—WC, 87, Co, 13 PER CENT. × 1500.
Last three etched with alkaline ferricyanide.

As the amount of tungsten carbide in the alloys is increased up to 97 per cent., no new changes in structure are noted; only an increase in the number of grains is apparent (Figs. 19–29).

FIG. 17.—WC, 40, Co, 60 PER CENT. × 1500.
FIG. 18.—WC, 45, Co, 55 PER CENT. × 1500.
FIG. 19.—WC, 50, Co, 50 PER CENT. × 1500.
FIG. 20.—WC, 55, Co, 45 PER CENT. × 1500.
FIG. 21.—WC, 60, Co, 40 PER CENT. × 1500.
All etched with acid ferric chloride.
FIG. 22.—WC, 65, Co, 35 PER CENT. × 1500.
Etched with acid ferric chloride + caustic electrolytic.

Several points in connection with the alloys of higher tungsten carbide contents are of considerable interest, from the standpoint of solubility. In the alloy containing 3 per cent. Co, the carbide particles are of very irregular shape, but with increasing cobalt content, the shape of these particles becomes more regular or angular.

Sometimes in cemented tungsten carbide there are material areas containing a large amount of binding constituent and little or no carbide. These have been designated as "lakes" (Fig. 30). The carbide particles adjacent to these lakes are all of regular configuration, and in some samples immense grains are noticed in what apparently had been lakes. These grains, too, are regular except where they touch (Figs. 31 and 32).

There is another method of making cemented tungsten carbide material which has the advantage of nearly instantaneous heat treatment. Consequently, there is a minimum of solubility taking place. The carbide particles in alloys made in this manner are very irregular in shape (Fig. 33).

INTERPRETATION OF RESULTS

There can be no room for doubt that considerable solubility occurs during the sintering of cemented tungsten carbide and cobalt. In the microexami-

27

29

FIG. 27.—WC, 92, Co, 8 PER CENT.   × 1500.
FIG. 28.—WC, 94, Co, 6 PER CENT.   × 1500.
FIG. 29.—WC, 97, Co, 3 PER CENT.   × 1500.
All etched with alkaline ferricyanide.

nation of this entire series of alloys below 35 per cent. WC content, there is no evidence of the original tungsten carbide particles. There is ample evidence of solution, indicated by the presence of the eutectic structures. Furthermore, all of the alloys below 35 per cent. WC, and also the surface layer on the pure cobalt, have fused during the standard heat treatment; so that up to a concentration of 35 per cent. WC the solubility of the carbide is sufficient to lower the melting point at least 80° C.

In considering the grain conformation as an indication of solubility, several photomicrographs might be brought to bear as evidence. The

FIG. 30.—WC, 95, Co, 5 PER CENT.   × 1500.
Etched with caustic electrolytic.

last operation in the manufacture of cemented tungsten carbide, previous to pressing and sintering, is a lengthy ball-milling operation. Micro-examination of this milled powder shows definitely that the particles are very irregular in shape. Fig. 33 shows a section of an alloy of 13 per cent. Co which has been sintered almost instantaneously. The carbide particles are very irregular.

Returning to the material of standard manufacture, the 3 per cent. Co alloy is composed of very irregular grains (Fig. 29); the 6 per cent. alloy (Fig. 28) and the 8 per cent. alloy (Fig. 27) begin to show geometric configurations in some of the grains. In the alloys of 13 per cent. Co, 20 per cent. Co, etc. (Figs. 25 and 26), increasing members of these grains are apparent.

FIG. 31.—WC, 94, Co, 6 PER CENT.　× 1500.
FIG. 32.—WC, 94, Co, 6 PER CENT.　× 4750.
Both etched with alkaline ferricyanide.

Referring again to samples containing "lakes" and areas of large regular shaped grains, it is evident that, given sufficient freedom, the grains of carbide present can, and do, grow. They tend to assume truly rectangular or triangular shapes, unless hindered by the presence of adjacent grains. Even in this event, the grains enlarge to their maximum allowable space and generally show curved contact surface with other grains (Figs. 31 and 32).

The maximum size of tungsten carbide particle that has been observed in the powdered raw material is about 20μ dia., and the maximum number of particles occur at about 2μ, these particles all being of irregular shape, due to ball milling. Consequently, when large, regular shaped grains are found, many times greater in size than 20μ, it seems conclusive that they must have grown.

With respect to one of the inconsistencies in the old conception of these materials, it has been previously noted that there had been observed in some alloys a much greater amount of binding constituent than could be accounted for by the cobalt content (Fig. 34). It seems to be invariable that whenever an extremely finely powdered carbide is used as a starting material, whether it be a carbide that has been produced as an extremely fine powder or has been reduced to such powder by ball milling, the resultant product has an unusually large amount of the binding constituent. This would seem to indicate that whenever very fine particles of tungsten carbide are present their solution in the cobalt is much easier and more rapid than that of coarser particles, giving rise to a greater amount of the binder.

Inasmuch as grains grow large under some conditions, they must be deriving their material for growth from the binder, and the latter must be obtaining this from the more easily dissolved small particles. Also, as the amount of cobalt increases, the average size of the carbide particles in the finished material increases, as can be seen in the accompanying photomicrographs. In conjunction with this, it is to be noted that in the alloys of 40 to 50 per cent. WC, wherein the carbide particles are nearly all formed by growth, the size is uniform, and generally of much greater magnitude than any initially introduced. There are practically none of the very small carbide particles present. All of this would point to the logical conclusion that, given freedom to grow and sufficient binder from which to draw material with which to grow, the ultimate size is dependent upon the factors of time and temperature.

An additional point of some importance concerns the structure of the matrix. As has been noted, the dendrites disappear at about 40 per cent. WC, and in all the alloys of greater content of tungsten carbide, the matrix is uniform and does not respond to the usual etching reagents.

Special efforts were made to etch an alloy containing 5 per cent. Co, and it was found that a grain structure could be developed in these

FIG. 33.—WC, 87, Co, 13 PER CENT.   × 1500.
FIG. 34.—WC, 92, Co, 8 PER CENT.   × 1500.
FIG. 35.—WC, 95, Co, 5 PER CENT.   × 3000.
Figs. 33 and 34 etched with caustic electrolytic; Fig. 35, with 50 per cent. hydrofluoric acid and 50 per cent. nitric acid.

"lakes" of binder, but the most that can be said is that apparently they are solid solution (Fig. 35).

Some important and corroborative data are obtainable from the preliminary X-ray studies of these alloys. All of the examinations to date show that there is a stretching of the cobalt lattice, even at the lowest carbide contents, and that there is no cobalt present as pure cobalt in any of these alloys. Both of these factors are in verification of the microscopic evidence.

The authors at present are of the opinion that the binding constituent in the cemented tungsten carbide materials usually reaches the liquid state during the final sintering operation, at which time it consists of tungsten carbide dissolved in cobalt. It is believed that upon solidifying this cobalt-rich cementing material remains as a solid solution of tungsten carbide in cobalt.

DISCUSSION

(S. L. Hoyt presiding)   .

Z. JEFFRIES, Cleveland, Ohio.—This paper presents in part a continuation of some of the ideas given to us in previous publications on cemented tungsten carbide, particularly some of the ideas expressed in Dr. Hoyt's lecture at the 1930 meeting in New York. It goes more into detail with reference to the variety of structures obtainable, and with reference to the nature of the cement than any work so far presented on the subject. The fact that the precipitation-hardening alloys deal essentially with equilibrium in alloy systems has been brought out. We only induce precipitation of hard particles by heat treatment when such precipitation tends toward phasial equilibrium in the alloys. Consequently, the number of alloys susceptible to improvement in hardness by age-hardening is limited, and the compositions are limited.

It has been further brought out that in the cemented tungsten carbide type of material we choose the quantities of the different constituents to suit the needs of the alloy. For example, we may choose 80 per cent. of tungsten carbide and put it into the mixture in the form of tungsten carbide particles. Then we may start with 20 per cent. of cementing material and heat to a desired temperature, and preserve the greater part of the tungsten carbide intact. In that way there is a wide range of compositions possible in these cemented alloys, which makes for a variety of results as regards hardness, toughness and other properties.

This paper brings out the importance of the study of equilibrium in the cemented alloy group. Equilibrium obtains in whole or in part in the cement only. The precipitation-hardening alloys usually possess reversible characteristics; that is, we may heat one of the precipitation-hardening aluminum alloys to 925° F., quench and then age-harden either at room temperature or some slightly elevated temperature. Then we may heat to an intermediate temperature—600° or 700° F.—and soften the alloy. To reharden, all that is necessary is to heat again to 925° F., quench and allow the material to age-harden under the proper conditions. We may do that time after time.

With these cemented alloys, a heating once to too high a temperature means that the relationship between quantity of cement and quantity of hard particle has been so changed that we cannot bring it back to the original condition. In other words, generally speaking, these alloys are irreversible in their heat treatment. In fact, by

completely melting one of these alloys and then solidifying, we may get different quantities of constituents and even different constituents from those which obtain in the properly sintered alloy.

This paper shows the great richness of structure obtainable in this type of alloy, and if the precipitation-hardening alloys have enriched nonferrous metallography to a great extent, and we all know they have, we may look forward in the future to still greater enrichment in type of structure, in variety of properties obtainable, and, in fact, to the enrichment of the whole field of metallographic science by the advent of cemented alloys.

W. P. SYKES, Cleveland, Ohio (written discussion).—This paper furnishes a most interesting and detailed description of the microstructures involved in alloys of cobalt and tungsten carbide. However, as the authors say, the conditions of temperature, composition, etc., maintained throughout the investigation rather limit the interpretation of the microstructures. It would seem that the composition of the cobalt-rich binding material must be governed by the extent to which the tungsten and carbon have diffused into the cobalt (liquid or solid) during the sintering operation.

FIG. 36.—PARTIAL PLAN OF TERNARY SYSTEM COBALT-TUNGSTEN-CARBON.

A current study of the cobalt-tungsten-carbon system has thus far yielded data which may be helpful in interpreting some of the microstructures shown in the paper under discussion. In Fig. 36 is presented a tentative diagram of part of the cobalt-tungsten-carbon system, constructed from the information furnished by melts of cobalt-tungsten and carbon cooled from about 1550° C. to various temperatures at various rates. Some cooling curves have been taken but exploration by this method is as yet incomplete.

In the pseudobinary series Co-W_2C, the second phase which occurs in a characteristic form best described as "herringbone" (Figs. 37 and 38) appears to have a composition represented by the formula $W_2C(Co)_2$. This is designated as β in Fig. 36. This phase can be formed as nearly 100 per cent. of the specimen by properly heating a mixture of cobalt and W_2C in the solid. It has a characteristic etching reaction as well as X-ray diffraction pattern.

When the W/C ratio approaches that for W_2C the β constituent appears to form a pseudobinary eutectic with the cobalt-rich solid solution. When melts of cobalt with from 10 to 30 per cent. of tungsten and sufficient carbon to exceed the W/C ratio of W_2C are cooled from 1500° to room temperature at a fairly rapid rate, the resulting structure appears to be that of cobalt-rich solid solution with a certain amount of ternary eutectic (Figs. 39 and 40). This ternary eutectic seems to be made up of the phase and graphite in a matrix of cobalt-rich solution. Reheating such an alloy at 1100° to 1200° C. for a few hours results in the formation of the WC phase, which appears to replace the β phase and graphite (Fig. 41).

Fig. 37-42.—Captions on opposite page.

A slower cooling rate from the molten state results in the formation of an apparent Co-WC eutectic in which the WC occurs as rods or needlelike crystals (Fig. 42). The range of composition and temperature in which these phases are stable has not as yet been accurately determined. It appears, however, that an unstable ternary eutectic exists in this region of the system composed of the β phase, graphite and a cobalt-rich solid solution. By reheating such a conglomerate to an intermediate temperature, a reaction occurs involving carbon and the $W_2C(Co)_2$ constituent to form WC. The WC formed in this manner is identified with certainty from its diffraction pattern, as well as its polishing and etching characteristics.

L. L. WYMAN.—The ranges covered by some of the structures in the paper agree very well with the graph and the description, or the interpretation, by Mr. Sykes. What we have characterized as white herringbone type of eutectic we first noticed at about 27.5 per cent. of tungsten carbide. In the samples treated under the regular manufacturing conditions, we noticed the last appearances of this in the neighborhood of 35 per cent. of tungsten carbide, covering a range of approximately 7.5 per cent. But by heating these alloys, in the one instance, for 20 hr., at a temperature of 1400° C., whether we slow-cool the sample from the moment of solidification or quench it from there, the structure is the same and shows a total absence of the white herringbone eutectic. This is in close agreement with Mr. Sykes' Fig. 36.

In the eutectic structure characterized in the paper as the arrowhead structure, which Mr. Sykes attributes to the tungsten carbide, the range covered is roughly from 30 to 45 per cent., and in all probability the lower figure is nearer to the composition at which this is probably stable.

FIG. 37.—Co, 71.0; W, 28.4; C, 0.6 PER CENT. × 1000.
Melt cooled 1500° to 1300° C. in 30 min. Quenched. Etched 10 per cent. HCl + H$_2$O$_2$, 0.2 amperes.
FIG. 38.—Co + 40 PER CENT. W + 1.5 PER CENT. C. × 200.
Melt cooled 1600° C. to black in about 3 min. Primary beta plus eutectic of cobalt plus beta. Etched alk. K$_3$FeCn$_6$. This etch produces film of brilliant colors on the beta phase.
FIG. 39.—COBALT + 20 PER CENT W + 1.22 PER CENT. C. × 200.
Melt cooled 1500° to 1300° C. 10 min.; 1300° C. to black in 2 min. Etched 20 per cent. Nitol. Cobalt-rich dendrites + ternary eutectic − (Co − beta graphite).
FIG. 40.—SAME AS FIG. 39. × 1000.
FIG. 41.—SAME SPECIMEN AS FIGS. 39 AND 40. × 1000.
Reheated at 1130° to 1140° C. 5 hr. WC replacing beta and graphite.
FIG. 42.—COBALT + 20 PER CENT. W + 1.5 PER CENT. C.
Cooled 1500° to 1200° C. in 1 hr. and quenched. Cobalt-rich solid solution + WC + few stringers of graphite.

Influence of Casting Practice on Physical Properties of Die Castings

By Charles Pack,* New York, N. Y.

Extensive progress has been made in the metallurgy of alloys for die castings. Enthusiastic proponents of some alloys are inclined to make extravagant claims for their materials, which may be justified by physical tests on test bars made from the respective alloys but are seldom justified by the results obtained with commercial die castings made from those alloys. Chemical analysis of the test bars and castings fails to determine the cause of these variations, since they are due to other physical factors entering into the commercial production of die castings.

In this paper, an attempt will be made to outline some of the factors in commercial die-casting practice to which these variable results may be attributed, in the hope that the manufacturer of die castings, recognizing the importance of these factors, will devote more attention to them in the design and construction of dies and equipment.

In 1914,[1] the author defined die castings as "metal castings made by forcing molten metal, under pressure, into metallic molds or dies." This definition was given in order to differentiate die castings from other molded metal products such as "permanent-mold" castings, "slush" castings and similar products that are sometimes erroneously termed die castings. The term "die casting" could be interpreted to include all castings made in metal molds or dies; but since this term, like most of our technical nomenclature, has been developed by commercial practice we must look to this practice for its proper definition. The Germans, with their usual devotion to descriptive names, have adopted the name of *spritzguss* (squirt cast) for die castings. Undoubtedly this name is more descriptive of the die-casting process, where the metal is literally squirted into the die and serves to differentiate this process from other metal mold processes, where the metal is poured into the die.

In the earlier paper mentioned, the author also emphasized the fact that the definition given for die castings indicated clearly that the satisfactory operation of the process must comprise three factors, all of which must be considered of vital importance to the successful operation of the die-casting process:

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[1] C. Pack: Modern Die-Casting Practice. *Trans.* Amer. Inst. Metals (1914) **8**, 87.

1. A casting machine or apparatus capable of holding molten metal and delivering it, under pressure, into the mold or die.

2. A suitably constructed mold or die.

3. An alloy suited to the machine and the die.

Each of these three factors has an important bearing upon the physical properties of the resultant product and if we add one other factor, the rate of cooling of the alloy, we have the four major factors entering into the production of die castings. A further analysis of these four major factors would permit of the following classification:

1. Composition of alloy.

2. Rate of cooling
{
 a. Casting temperature.
 b. Temperature of die.
 c. Wall thickness.
}

3. Casting machine
{
 a. Pressure.
 b. Gate.
 c. Speed of operation.
}

4. Die
{
 a. Gate.
 b. Vent.
 c. Fillets.
 d. Ribs and bosses.
 e. Core removal.
 f. Condition of die.
}

COMPOSITION OF ALLOY

The effect of variations in composition on the physical properties of die castings is now being investigated by a committee of the American Society for Testing Materials and the results of this investigation, when published, will cover this subject thoroughly. The writer will therefore confine himself, in this paper, to the subjects outside of alloy composition that may affect the physical properties of die castings.

RATE OF COOLING

The importance of regulating the rate of cooling in foundry practice is well known. The possible variations in the rate of cooling are much greater in die-casting practice and the control of the cooling rate is far more difficult. Furthermore, the zinc-base alloys, which are extensively used in die-casting practice, are of a highly crystalline nature and are dependent upon rapid cooling for their useful properties. Variations of over 25 per cent. in the physical properties of zinc-base die castings may be attributed entirely to variations in the rate of cooling during the casting operation. These variations are due mainly to casting temperature, temperature of die and wall thickness.

Casting Temperature.—The importance of this factor in foundry practice has been studied and recognized. It is of equal importance

in die-casting practice, particularly since some alloys have a tendency to develop hot-shortness at elevated temperatures. The rule that has the most general application is the following: The best casting temperature for any alloy is above the melting point, but as near as possible to the melting point of the alloy.

So many other factors enter into the production of die castings that it is not always possible to adhere to this rule. These factors, which are mainly mechanical, will become more apparent later in this paper. In commercial practice, casting temperatures are often raised above the known optimum, because it presents the simplest method of overcoming visible defects. It is the easy method of solving many die-casting difficulties, but far from the best. The best results will be obtained if the plant metallurgist will establish a definitely known optimum casting temperature and insist that this temperature be maintained in practice.

Temperature of Die.—This factor is even of greater importance in its influence on the physical properties of a die casting than is the casting temperature of the metal. As a general rule, the more rapid cooling of the metal will result in castings of the best physical properties. The operating temperature of the die is the most important factor in controlling the rate of cooling of the metal and it follows therefore that the best physical properties may be expected when the die is operated at the lowest possible temperature. Unfortunately, this rule also cannot be taken literally, without considering the other factors that enter into the process; more particularly is this rule tied up with the speed of operation of the machine, as will be seen later.

Wall Thickness.—It is self-evident that, all other factors being equal, the physical properties of a die casting will vary with the cross-section of the casting, and proportional lower physical properties may be expected as the wall thickness of the casting increases, due to the slower rate of cooling of the heavier casting. Furthermore, the possibility of blowholes due to trapped air and shrinkage voids becomes much greater as the wall stock increases, which also tends to reduce the average physical properties of the casting. The typical structure of a die casting is a dense, close-grained outer section, the grain becoming coarser towards the center of the section, often with visible pinholes in the center of the heavy sections.

CASTING MACHINE

The design and construction of the die-casting machine limits the type of alloy that can be used in the process. The variation in the types of die-casting machines used in commercial practice are responsible, to a large extent, for the variation in alloy practice among the various manufacturers of die castings. The type of casting machine also has an important bearing on the physical properties of the castings produced, as will be shown hereafter. The particular items in machine design that

influence the physical properties of the resultant product are pressure, gating and speed of operation.

Pressure

Assuming that the best physical properties may be obtained with a comparatively cold die and low metal-casting temperature, it naturally
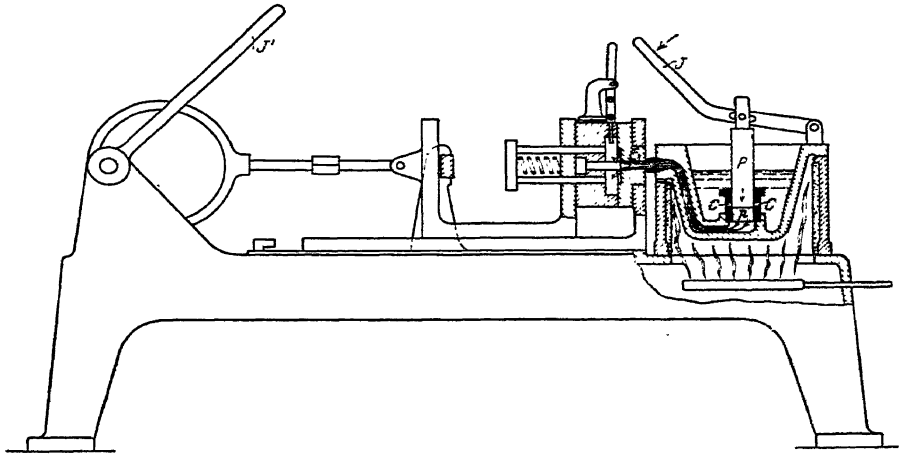
FIG. 1.—TYPICAL PLUNGER MACHINE IN CASTING POSITION.
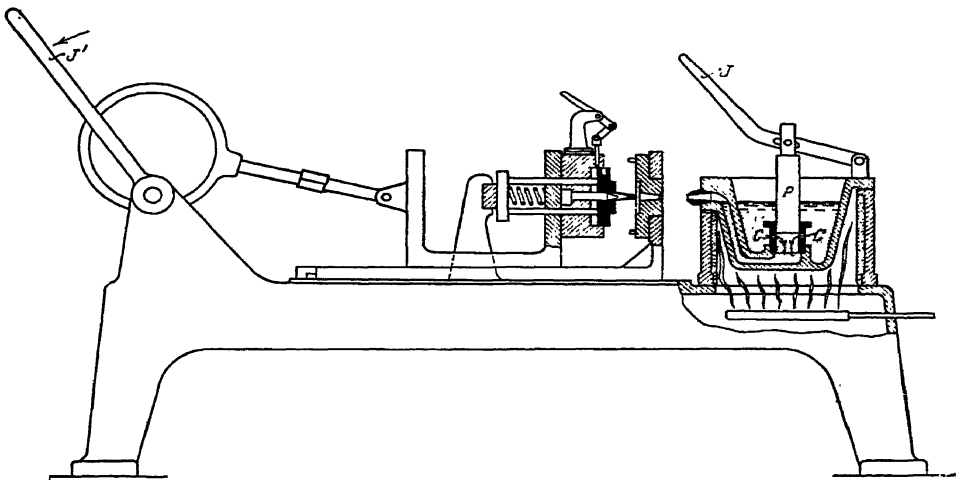
FIG. 2.—TYPICAL PLUNGER MACHINE READY FOR EJECTION OF CASTING.

follows that, in order to maintain these conditions, the metal must be forced into the die under high pressure. Many manufacturing problems of die-casting plants may be directly attributed to lack of sufficient pressure behind the metal.

Two types of die-casting machines are generally used in this country: (1) the plunger machine and (2) the direct air machine.

The plunger machine was the first type used.   It originated with the development of the linotype machine in the printing art which today embodies an automatic die-casting machine developed to its finest point. This machine, an example of which is illustrated in Figs. 1 and 2, derives its pressure by the operation of a piston in a cylinder immersed in the
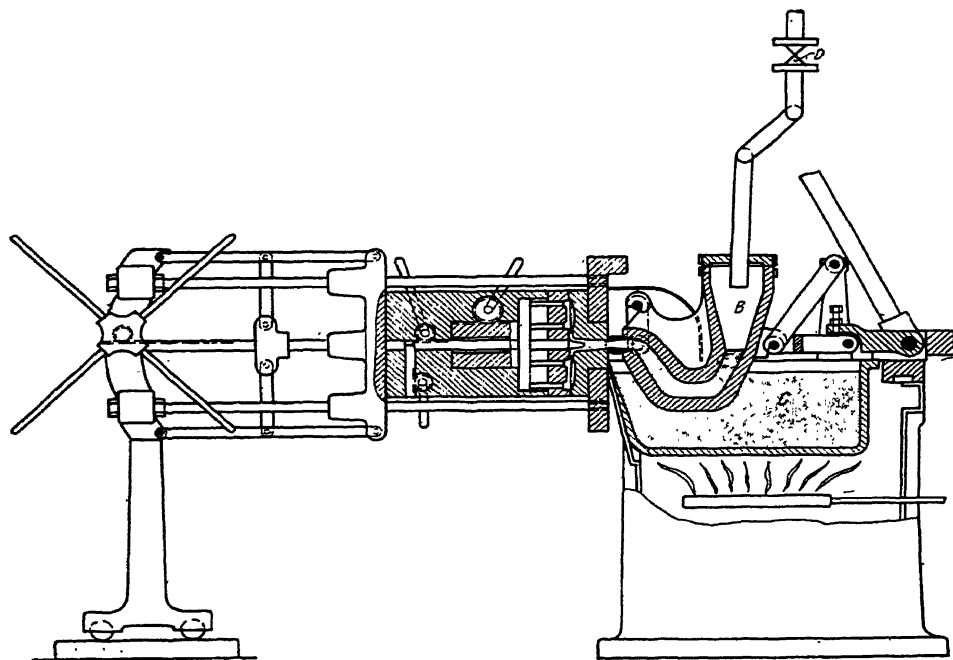
FIG. 3.—TYPICAL GOOSENECK MACHINE IN CASTING POSITION.

molten metal.   Fig. 1 shows this machine in operating position, the die being closed and ready to receive the molten metal.   By applying force to the lever J the piston P is forced downward, closing the ports C and forcing the metal ahead of the piston into the die.   In this illustration, a hand lever is shown for operating the plunger but in modern practice the plunger is operated by pneumatic, hydraulic or direct mechanical power.   The advantage of this type of machine lies in the fact that it is possible to produce any desired pressure by the application of the required force behind the operating plunger P.   Its main disadvantage lies in the fact that at casting temperatures of over 850° F. there is a tendency for the plunger to "freeze" in service, which precludes its use for aluminum and copper-base alloys.   The plunger shown in Figs. 1 and 2 operates

in a vertical direction but similar machines are in use with plungers operating in a horizontal direction.

For the casting of aluminum, machine designers discarded the plunger type of casting machine and the direct air machine was developed. This type of machine may be said to be used exclusively in this country for the manufacture of aluminum-base die castings and to an appreciable extent also for the manufacture of zinc-base die castings. A machine
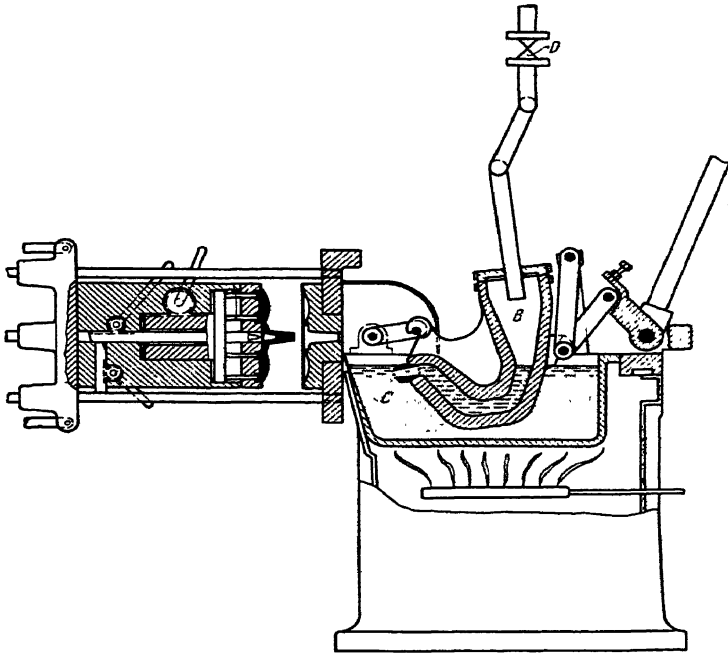
FIG. 4.—TYPICAL GOOSENECK MACHINE SHOWING FILLING POSITION OF GOOSENECK.

of this type, commonly known as the "gooseneck" machine, is illustrated in Figs. 3 and 4. Here the metal is maintained molten in a reservoir C. Operating in this reservoir is the gooseneck B which may be locked to the die when in the casting position (Fig. 3) or dropped into the reservoir (Fig. 4). In Fig. 3 the gooseneck is shown in its position ready for casting, which is accomplished by opening the valve D. This permits the high-pressure air to impinge on the surface of the metal in the gooseneck, forcing the metal into the die. The air is permitted to escape into the room after each casting operation, through an exhaust outlet provided for that purpose. The gooseneck is then dropped into the position shown in Fig. 4, when the metal discharge nozzle at the end of the gooseneck becomes an inlet nozzle, because it permits the metal to flow into the gooseneck by gravity. Machines of this type are operated under pressures varying from 250 to 500 lb. per sq. in. It is doubtful

whether it would be practical to operate this type of machine at much higher pressures. Although air pressures up to 1000 lb. per sq. in. are being used in other industries, the use of such pressures in this type of machine would prove dangerous and expensive.

On the other hand, it is entirely practical to operate plunger-type die-casting machines with nozzle pressures exceeding 5000 lb. per sq. in. It would seem, therefore, that where the plunger type of machine can be used, the best results will be obtained with this type of machine. The use of the direct air type of machine for casting aluminum alloys is based on the theory that the plunger principle cannot be applied to the casting of aluminum alloys. Recent developments in design prove the contrary. There can be no doubt that the future development of the aluminum die-casting industry must be limited if the manufacturing process will be limited to operating pressures of 500 lb. The writer is of the opinion that the future die-casting machine will be built around the plunger principle rather than the direct air, not only for the alloys of zinc but for the alloys of aluminum and copper as well. Machines of this type are now operating commercially and the writer hopes to be in a position to describe them in greater detail at a later date.
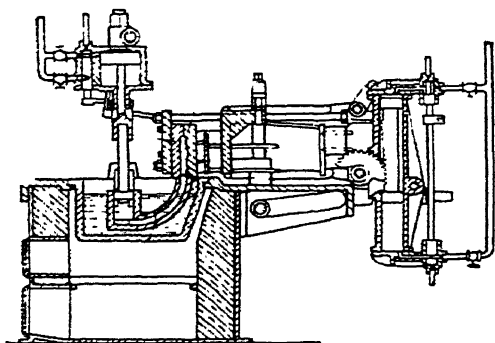
FIG. 5.—DIE-CASTING MACHINE SHOWING SIDE-GATE PRINCIPLE.

Methods of Gating

Two general principles of gating are used in die-casting practice and the type of gate used is determined by the design of the casting machine. The machines illustrated in Figs. 1, 2, 3 and 4 are built around the center gate principle. In these machines the metal enters the die through an opening provided in the center of one-half of the die. In the machine shown in Fig. 5, the metal enters the die through the parting line of the die, at one end of the die. This is commonly called a "side gate."

There is much to be said in favor of both of these methods of gating. In some instances the side gate is highly desirable, but these instances are not numerous, and the use of the enter-gate principle predominates in die-casting practice. Many users of side-gate machines have discarded this practice and have adopted the center-gate principle.

Speed of Operation

Although not readily apparent, it is nevertheless true that the speed at which a casting machine operates, or, to be more exact, the time that

elapses between the injection of the metal into the die and ejection of the casting from the die, has a vital bearing on the physical properties of the resultant castings. In order that we may more readily appreciate the importance of this time factor, it may be advisable to consider the physical reactions that take place in the process of die casting.

When the metal is forced into the die it solidifies instantly and that solidification is accompanied by a reduction in volume, commonly called shrinkage. Although the designer of die-casting dies allows for what he terms "shrinkage," it is physically impossible for the casting to contract while it is in the die. The casting is surrounded by the solid, incompressible steel and the shrinkage incident to the solidification of the metal is converted into a tension strain on the casting. The alloy must "stretch" sufficiently to compensate for this reduction in volume.

The metal having solidified and shrinkage having taken place, a further reduction in volume takes place, due to the cooling of the casting from its melting point down to the temperature at which it is removed from the die and from that temperature to room temperature. The only shrinkage that we can obtain in die-casting practice is that obtained incident to the cooling of the casting, after it has been removed from the die.

If we were to make a casting in a die and permit it to remain in the die until it had cooled down to room temperature, naturally, we would find that the dimensions of the casting conform to those of the die cavity. The reductions in volume incident to solidification and cooling have been converted into tension strains that have "stretched" the casting to the dimensions of the die. This, of course, does not apply to shapes that are unrestricted in shrinkage in the die, such, for example, as the diameter of a solid disk. Such parts are seldom met with in commercial practice, however.

It seems evident that castings permitted to cool in the die must be placed under tremendous strains and the tensile strength of such castings must suffer materially. Most commercial die castings from zinc-base or aluminum-base alloys if permitted to cool in the die to room temperature would come out of the die badly cracked. This is undoubtedly due to the fact that the alloy is unable to withstand the strains imposed, incident to solidification and subsequent cooling. It is usual for the first castings made from a cold die to be badly cracked. After the die has been run for some time, the cracks may disappear, because the die has "warmed up" and the castings are being removed from the die at a higher temperature. It would follow therefore that it would be most desirable to remove the casting from the die at the highest possible temperature.

Assuming the casting temperature and the temperature of the die to be constant, it is evident that the temperature at which a die casting will be removed from the die must vary directly with the speed of opera-

tion.   Since it has already been shown that the best results are obtained with low casting temperatures and cold dies, it follows that in order to maintain these conditions we must have speed of operation or the beneficial effect of the rapid cooling of the metal is more than counteracted by the detrimental effects of cooling the casting within the die.   We can now summarize the most desirable operating conditions of a casting machine from the standpoint of obtaining the maximum physical properties from the resultant product, as follows: (1) Low casting temperatures; (2) cold die; (3) high pressure; (4) rapid ejection from the die.

It also follows that with a machine that operates slowly it is best to operate the die at a higher temperature, because the reduction in the speed of cooling is not as harmful to the physical properties of the castings as the stresses set up within the castings when they are permitted to cool down to too low a temperature in the die.   With a fast machine it is possible to obtain better castings, since it is possible to operate with a comparatively cold die and eject the casting from the die before it has cooled to any appreciable extent.

We may also conclude, from the foregoing, that under a given set of operating conditions, the alloy that will produce the most satisfactory die castings is the one that is best able to withstand the strains set up incident to the solidification and cooling of the metal in the die.   The failure of an alloy to meet these conditions may be termed "hot-shortness," and is of the greatest importance in determining the adaptability of any given alloy to die-casting practice.

DIE DESIGN

The designer of the die-casting die can influence the ultimate strength of a die casting by the proper or improper design of any particular die, since the very best alloys and the best operating conditions will not insure the quality of the resultant product unless the die is also constructed to conform with the best die-casting practice.   Furthermore, the die designer, familiar with the theories and principles of good die-casting practice, is in an excellent position to recommend minor changes in the design of the die-cast part, which may often be of major importance in determining the ultimate strength of that part.   It is not within the scope of this paper to attempt a detailed discussion of die construction but only to point out briefly those factors in die design and construction which have an apparent effect upon the physical properties of die castings.

The Gate

It has already been pointed out that the type of casting machine used controls to a large extent the basic type of gate that may be employed, but the die designer can aid materially in producing strong castings by careful attention to each gate within the die proper.   Upon the proficiency

in gating will depend to a large extent the number of blowholes, dross inclusions, etc., that will occur in the castings. As a general rule, given a machine with ample working pressure behind the metal, the gate inlet to the casting proper should be as small as possible; a long thin gate usually is preferable to a short wide gate. No universal rule of gating can be laid down that will apply equally to all types of casting machines and the infinite variety of castings that must be considered.

Some attempts to lay down definite principles of gating die-casting dies have been made. Frommer[2] has given some detailed data on the direction and velocity of the flow of the metal in a die-casting die. It is the writer's opinion, however, that the theories outlined would not apply equally to all types of casting machines. The proper gating of a die cannot be accomplished by any hard and fast rule. The skilled die designer will lay out the gate in the die after a careful study of the direction of the flow of the metal in that particular die. After the die has been constructed he will check up on his theory and determine, if possible, just how the die is being filled. For this purpose, the writer has employed a method that may prove of value to other experimenters with die-casting gates.

In order to determine the direction of the flow of the metal in the die, a mixture of heavy oil and graphite is injected into the nozzle of the casting apparatus or into the main gate hole of the die. The casting is then made with a restricted pressure. By varying this pressure it is possible to obtain castings either partly or entirely filled out but the flow of the metal will be indicated clearly by the dark streaks left by the oil and graphite in the casting. With this method it is possible for the die designer to locate air traps and other objectionable conditions that will have a detrimental effect upon the physical properties of the castings.

Fillets

When a casting of the section illustrated in Fig. 6 cools in the die, the main shrinkage and cooling strains set up will be concentrated upon the weakest point in the casting, which in this instance would be the points A and A'. If we strengthen these two points by the addition of metal in the form of fillets, the shrinkage strain will tend to be distributed over the entire horizontal section of the casting. Without fillets we may reasonably expect cracks in the corners if the die is operated slowly. With rapid die operation or with the die at high temperatures we may eliminate the visible cracks but the casting would be greatly weakened at these points. The value of fillets is appreciated in foundry practice, but they are of far greater importance in die-casting practice. The practice of

[2] Von L. Frommer-Charlottenburg: Der Spritzguss. Werkstattstechnik (1926) **120**, No. 4, 99.

casting sharp V-threads also tends to weaken the casting at the threaded area.

Ribs and Bosses

It has already been noted that in cooling of the casting section illustrated in Fig. 6 the shrinkage strains will be concentrated at the points A and A'. The amount of strain exerted at these points will be in direct proportion to the length AA', provided no projections are cast between the points A and A'. If we should add a rib B (Fig. 7) halfway between the points A and A' it would tend to retard the shrinkage between the points A and A' and reduce the shrinkage strain by one-half. We may go further and add more ribs between AB and $A'B$ to further divide the shrinkage and proportionally reduce the strains set up in casting, and tend thereby to produce castings of better physical properties. Bosses may also be used to break up shrinkage strains where ribs cannot be used.

FIG. 6.—FORM OF CASTING THAT REQUIRES FILLETS.
FIG. 7.—RIB PLACED TO REDUCE SHRINKAGE STRAIN.

Core Removal

With castings having large cores, the die designer has the option of providing means of withdrawing the cores immediately after casting or ejecting the casting off the core by means of ejector pins provided in the die. Cores should be removed from the casting as rapidly as possible in order to obtain castings of maximum physical properties.

Condition of Die

The physical properties of die castings may be greatly reduced by strains set up in the castings through the improper ejection of the castings from the die. Improper ejection may consist of improper alignment of the ejector mechanism of the die, undercuts, insufficient taper, burred or nicked edges or any other condition existing in the die that may tend to make the ejection of the casting from the die more difficult.

Poor die-casting practice may often result in cracked castings, but the fact that a casting is free from visible cracks is no indication that it is a good casting. Carelessness and indifference as to the condition of the die may result in castings which show no visible cracks but which may have been strained almost to the point of rupture in the die-casting process. Undercuts, burred edges, insufficient taper, uneven ejection and other defects in the die will leave visible marks on the castings in the form of "rubs" or "drags," which are readily distinguishable. The presence of

such "rubs" or "drags" on the castings are certain indications that these castings are being unnecessarily strained in the process of ejection from the die.

CONCLUSION

It has been the prevailing belief that the physical properties of die castings are dependent entirely upon the composition of the alloy used. Deviations in the physical properties of die castings have been promptly attributed to alloy variations and it has been rather difficult for the plant metallurgist to enlist the cooperation of those responsible for machine and die design, in his efforts to produce die castings of better physical properties. The writer hopes that by this paper he will have helped to emphasize the fact that the production of good die castings that will meet maximum physical requirements is not entirely within the control of the plant metallurgist, but that this responsibility must be shared equally by the mechanical and metallurgical divisions of the plant.

The present die-casting industry has been built upon the principle that the mechanical phase was predominant. Mechanics designed the die-casting machine and the die for use with the machine, leaving it to the metallurgist to provide suitable alloys. Under these conditions, the metallurgist was greatly limited in his choice of alloys. The writer is pleased to record a growing tendency to recognize the importance of the metallurgical phase of the industry in designing die-casting machines. Future development of die-casting equipment may be expected to comply with good metallurgical practice.

DISCUSSION

(W. R. Webster presiding)

F. J. TOBIAS, New Haven, Conn. (written discussion).—It is always refreshing to read a statement by an authority that all the troubles occurring in the making of die castings are not to be attributed to alloy questions alone, and that casting machines and die and the cooperation between metallurgist and maintenance engineer are most essential to secure best results. From this angle the paper by Mr. Pack certainly is a valuable addition to the literature dealing with die castings.

Referring to his paragraph on casting machines (p. 232), it may be mentioned that die-casting concerns in general have the advantage of possessing different types of die-casting machines in regard to size and construction and in this way solve more easily the problem of putting the right job on the right type of machine.

The trouble encountered with die-casting alloys in the past has been considerably reduced. A list of approximately 35 different zinc-base alloys and 25 different aluminum-base alloys has been advantageously reduced to approximately 2 zinc-base alloys and 3 aluminum-base alloys.

Mr. Pack seems to be in favor of the center-gate type of machine. It is an advantage to have both center-gate and side-gate types of machines in a die-casting plant. Especially, the side-gate machine has the advantage of having less gate and fewer fins than the center-gate machine. This question is of great interest to the foundrymen who have to solve the problem of getting rid of gates and overflows without reducing the quality of the metal. This is a point worth considering. Also, the

material of which the dies are made is more abused in the center-gate machine than in the side-gate machine.

On page 239 Mr. Pack suggests a way to determine the direction of the flow of the metal in dies. We must not forget the rather more accurate method of X-rays or radiographs. Extensive experiments have been made by Isenberger & Co., and very interesting also is the paper by Fink and Archer.[3]

On the same page Mr. Pack advocates strengthening castings with ribs and fillets, and cautions against weakening by casting in V-threads. The user of die castings should not forget that the die-casting industry is in a position to strengthen castings considerably by casting in inserts and, if necessary, inserts with threads where such a procedure is desirable.

S. Tour, New York, N. Y.—On page 239 Mr. Pack says that long, thin gates are usually preferable to short, wide gates. I agree with him on that but not on the statement that the gate inlet should be as small as possible. Choking down the inlet too much—in other words, cutting down the area of the inlet too much—spoils the effect of added pressure on the pressure end of the machine. There is no reason for going up to figures of 5000 lb. per sq. in. pressure if the gate is to be so constricted that that pressure never gets into the die cavity.

In the same paragraph, Mr. Pack refers to a method of checking up the way in which metal enters a die, by using oil and graphite in the die and then making a casting with restricted pressure and looking at the casting afterwards to see the flow marks. A decrease in pressure in this manner decreases the velocity of metal as it goes through the gate; therefore it cuts down the distance to which that metal will squirt as it leaves the gate. The picture given by this method, using oil and graphite, is entirely different from the true picture of the way the metal actually does enter with high pressure. The only method I have found which really does tell how the metal is filling the cavity is a study of the finished casting produced under production conditions by means of X-rays.

With regard to fillets, Mr. Pack makes the statement that weakness in castings is due to shrinkage strains, which do not break the casting but stress it an unreasonable amount. I question the statement that a casting which has been stressed, even beyond the elastic limit in the hot state, is going to be materially weaker after it cools down. The metal stretches or elongates in the die, and it does not follow that because of this the metal is weaker at room temperature after it comes out of the die than if it had cooled in the die unrestricted and been allowed to shrink.

He claims that he cuts down the amount of shrinkage by the use of ribs and bosses. As a matter of fact, the use of ribs and bosses, instead of cutting down shrinkage, simply distributes shrinkage, preventing its becoming localized at one sharp corner, causing the casting to crack.

E. A. Anderson, Palmerton, Pa.—Mr. Pack has done well to call attention to the necessity of defining casting conditions to secure the optimum conditions for the best properties. I should like to take issue with him, though, on one point, which is the question of die temperature. The original physical properties possibly are improved somewhat by decreasing the die temperature, but the zinc-base alloys now in use are all in a metastable condition when cast and undergo a slow transformation, with some slight alteration in dimensions and properties. This alteration is dependent somewhat on the temperature of casting. The lower the die temperature, the greater will be the amount of alteration in a given period of time, and I would rather suggest a little higher temperature to insure the minimum change in properties.

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[3] W. L. Fink and R. S. Archer: Radiography as a Tool in the Metal Industry. *Trans.* Amer. Soc. Steel Treat (1929) **16,** 551.

C. Pack (written discussion).—Mr. Tobias' discussion is of more than average interest in view of his extensive experience in the die-casting art. I feel, however, that I have not made myself quite clear on one or two points discussed by him.

Mr. Tobias says that the alloy troubles of the past have been materially reduced by reducing the number of zinc-base and aluminum-base alloys from approximately 60 to 5. No one can dispute the value of standardization of alloys and the elimination of useless alloys, but I feel that the die-casting industry of today is entirely too restricted by the comparatively few alloys that can be cast. The die-casting industry of the future will have no special alloys; it will simply be a method of casting all metals and will not be limited to 5 or to 60 alloys, any more than the sand foundry. It would be somewhat difficult to enter into more details in this discussion but I have written (June, 1931) a paper for *Metal Progress* which will appear in that publication very shortly and which describes more clearly the future die-casting industry.

Mr. Tobias has gained the impression from my paper that I favor the center-gated casting machine. I wish to correct this impression. I fully agree with Mr. Tobias that there is a distinct advantage in having both the center-gated and side-gated machine in the same plant. Both have distinct advantages on some specific jobs. I intended merely to state the fact that the center-gated casting machine is more extensively used in commercial practice and that this type of casting machine is more generally applicable. I cannot, however, agree with Mr. Tobias that center-gated dies are more abused in production than end-gated dies. The life of a die does not depend upon the type of gate used. I have seen side-gated jobs that showed premature die failure where the job showed to much better advantage with a center gate. The design of the die and the many other factors I have pointed out in my paper have a more far-reaching effect on the die life. There are some instances where a die may show up to better advantage when side-gated but I cannot concede the statement that die life, in general, is materially affected by the center or side-gate principle.

I am glad that Mr. Tobias mentioned the use of the X-ray for determining the flow of metal in a die-casting die. The metallurgist, however, is often called upon to decide quickly on a change in gating, and the method described in my paper affords a possibility of studying on the job the metal flow in the die, and enables him to take prompt action when necessary. I used the method outlined in my paper long before the X-ray was developed as a research instrument and often it has enabled me to produce satisfactory castings with the least possible delay. My method is not intended to replace the X-ray, nor is it as positive in its results as the X-ray, but often it will save the day when results are needed quickly and time does not permit an X-ray study, particularly when the equipment is not available in the plant.

Mr. Anderson says that it is not advisable to cast some of the zinc-base alloys with a cold die. This is true with some of the zinc-base alloys used at the present time. There are some zinc-base alloys, however, that show to best advantage when cast in a die maintained at as low a temperature as possible. I made the statement that as a general rule the lower die temperature will produce castings of higher physical properties, but I pointed out that this rule must not be taken literally and that there are other factors, far more important, that may make it advisable to use higher die temperatures. In stating this rule, I had other alloys in mind, such as copper, aluminum and magnesium-base. I have found large variations in the physical properties of opposite ends of the same test bar that could be attributed only to the variation in temperature of the die. Furthermore, I have obtained results with aluminum alloys that prove conclusively that when these alloys are cast in a cold die the physical properties are materially improved.

Mr. Tour has emphasized the fact that reducing the gate to a point where it "chokes" the inlet tends to nullify the effect of the pressure used. In making the statement that long, thin gates are to be preferred to short, wide gates, I merely stated

what is general practice in the art. I am not in agreement with this practice. The reason for the necessity of the thin metal inlet is generally twofold: (1) With a thick gate section, the possibility of striking blowholes when removing the gate is materially increased. Given a machine that will deliver uniformly solid metal to the gate of the casting, it would be possible and very often highly desirable to use a thicker gate that would not restrict the flow of the metal and tend greatly to reduce shrinkage voids; (2) the thick gate is more costly to remove and often may involve an additional operation. This consideration is secondary, however, when considered from the standpoint of quality production.

The designer, however, is often faced with the problem of gating a casting at a thin section. This may be made necessary by practical die construction. Here the higher pressure will be of material advantage.

Mr. Tour is of the opinion that a casting stressed even beyond the elastic limit in the hot state will not be materially weaker than a casting of the same alloy that has not been subjected to this strain. I cannot agree with Mr. Tour on this point and I submit herewith some facts that have influenced my opinion.

It is generally recognized that thin sections of a die-cast part are proportionally stronger than the heavier sections. In the A. S. T. M. program, two types of tensile bars were used, a flat $\frac{1}{8}$-ft. and a round $\frac{1}{4}$-ft. bar. It was generally expected that the flat bars would show better physical properties but in most instances the round bars showed up better. I believe that this is due entirely to the fact that the flat bar was unable to resist the shrinkage and cooling stresses as well as the round bar. If there is any other explanation for the peculiarity of the results obtained with the flat test, I would be much interested in it.

Recently I made some extensive experiments, with a large variety of alloys, with a pressure casting machine and a die containing all three of the standard A. S. T. M. die-cast test bars—flat, round and square. The three bars were cast in the same die, in the same operation. The alloys were copper-base, aluminum-base, magnesium-base, zinc-base and cadmium-base alloys. I believe that the alloys cast in these experiments had the widest possible variations in physical properties, both in the hot and cold state. It is peculiar that in these experiments the physical properties were generally higher on the round bars than on the flat. The exceptions to this rule were found in the alloys that are known to be notably free from hot shortness. The 13 silicon, 87 aluminum alloy will serve as an illustration. With this alloy the flat test bars were uniformly stronger than the round bars. The results of these experiments convinced me that the flat bar was useless as a test of the tensile strength but indicated rather the hot shortness of the alloy. However, by determining the tensile strength of the flat and round bars of any given alloy and comparing the difference between these results with the difference of the results between the flat and round bars of any other alloy, I found that I could get a somewhat definite comparison of the hot-shortness of the alloys. For example, it is well known that the 13 silicon, 87 aluminum alloy is less hot short and will resist shrinkage stresses much better than Y alloy. On these alloys I obtained the following results:

	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Impact Toughness, Ft-lb.
87-13 alloy, flat	44,440	4.5	5.26
87-13 alloy, round	41,640	4.3	4.5
Y metal (as cast), flat	34,550	2.6	5.4
Y metal, round	38,260	3.4	5.8

It is evident that the physical properties of the flat bar are higher than those of the round bar with the silicon alloy. This is one of the exceptions, however. If the stresses set up incident to the shrinkage and cooling of the metal in the die has no effect on the ultimate strength of the resultant castings, we should reasonably expect to find that the results with all of the alloys should parallel those obtained with the silicon alloys, inasmuch as the flat bars should give higher results than the round bars.

Mr. Tour is correct in his statement that the use of so-called shrinkage ribs and bosses do not cut down the shrinkage. The shrinkage value of any given alloy is a fixed quantity that cannot be altered. These ribs and bosses can be used, however, to distribute the shrinkage and reduce the stresses at any given point in the casting, in order to eliminate so-called shrinkage cracks. This practice is so extensively used that it requires no further discussion here.

Fabrication of the Platinum Metals

By C. S. SIVIL,* NEWARK, N. J.

To modern civilization the platinum metals are of inestimable value. Their distinctive properties, both physical and chemical, render them indispensable in an age in which the processes of the laboratory are becoming an essential part of the daily life of the world. Generally, their function, though vital to particular processes, is not spectacular, and so remains unknown to all except the operators.

EARLY METHODS OF MANUFACTURE

The properties of platinum were recognized as of prime importance for scientific work at a very early date, probably between 1750 and 1760. The difficulty of making articles from it seemed almost insurmountable, because no means of attaining the temperature necessary to melt it were known at that time. It is true that solid platinum could be obtained by fusing the metal with a more volatile metal such as arsenic, which was subsequently driven off by baking, but such a method, at its best, would give only a very brittle product, which was totally unsuitable for the purposes for which it was intended. Little, if any, progress could be made until it was discovered that platinum sponge, heated to white heat and hammered in an iron or clay mold, would metallize and retain the shape of the mold. This was a process that could not be wholly satisfactory but from it developed the method of pressing the sponge in a mold and forging it at white heat into wire or sheet. At present a somewhat similar process must be used for fabricating articles of tungsten, molybdenum and other metals of high fusing point, as with these metals we face today the same problems that the scientists of the eighteenth century encountered with platinum, but possibly the next significant advance in the metallurgy of these metals will be the devising of means to melt and cast them.

To some extent this method of preparing platinum has survived, particularly in Europe. There are one or two objections to it, but they are not serious, as they can be surmounted with proper precautions. In the first place, the material is spongy and its millions of cavities contain entrapped air. Unless this is removed by thorough forging above 1000° C. the resultant sheet shows blisters. To give such a thorough forging,

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* Baker & Co., Inc., Research Department.

bars of large cross-section are necessary and this leads to trouble of a different nature. If the bar is too large the friction at the side of the mold becomes important, and a large bar, so produced, is of varying density and either warps and fractures when heated or shows shrinkage holes at the least dense points, resulting in large blisters or double stock.

The pressures involved in this process are not great. The writer has found that between 30 and 40 tons per square inch produces a bar that has a density of 20 to 20.5 grams per cubic centimeter. The appearance of the bar is metallic and it has remarkable strength, as it can be cold-hammered to some extent. In a cross-section polished and etched the material appears to be structureless. This recalls Beilby's[1] experiments with gold powder, which assisted him in his formulation of the theory of the vitreous amorphous state.

A third objection to the sintering process is that it does not assist in the refining of the metal. In melting, base metal impurities can be oxidized and slagged away and volatile impurities can be removed. This objection, however, is weak, as the art of refining by chemical methods has advanced to such a state that it is unnecessary to rely at all on this refining action. Sponge with only spectrographic traces of impurities is now a regular product of chemical refining.

Scrap metal cannot be recovered by sintering, and it is here that melting shows its greatest advantage, as the cost of responging the scrap is much higher than that of remelting it. Melting also can deal with much larger quantities, as we do not encounter the obstacles, mentioned above, that confront us when pressing any considerable amount of the metal at one time.

In the manufacture of rhodium and iridium and certain alloys which tend to dissolve gases, sintering is relied on, even today, for sure results, but research is being directed towards suitable melting methods for the same reasons as were outlined for platinum.

Melting Platinum

In 1802, Robert Hare, of Philadelphia, invented the oxyhydrogen blowpipe. This invention was revolutionary in the metallurgy of platinum and still retains its importance in the art. In 1856 Deville and Debray improved the application of the blowpipe by hollowing a crucible out of lime and using a lime block for a lid, and this is the method of melting used today. The fuels used are mainly hydrogen or city gas but almost any gaseous hydrocarbon can be used. On account of the remarkable solvent powers of these metals for gas the flame composition is very important. On this subject, as Carter has pointed out,[2] the literature is

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[1] G. T. Beilby: The Aggregation and Flow of Solids. London, 1921. Macmillan

[2] F. E. Carter: The Platinum Metals and Their Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 759.

very confusing. Apparently minute amounts of certain impurities influence to a tremendous extent the capacity of the metal to absorb gases and affect the physical and chemical properties of the metal. It is probable that the property of absorbing gas is the cause of the value of platinum as a catalyzer of gaseous reactions and it is easy to see that if the solvent power of the platinum is diminished its value as a catalyzer is consequently diminished. This may explain the poisoning effect of certain elements on catalysts.

Research is being directed towards not only the determination of the gases dissolved but also the determination of their quantity. By an ingenious application of the electric discharge in a vacuum, Stauss[3] has been able to show that the gas dissolved in platinum is oxygen. A discharge tube was constructed into which a coil of wire or a piece of sheet could be introduced. Exhaustion was carried out until no discharge passed and the tube was then shut off from the pump. The metal was heated by high-frequency induction and immediately the discharge commenced to pass, the color being characteristic of oxygen. By determination of the pressure in the apparatus before and after degassing, the quantity of gas removed can be found.

The effects of oxygen on the physical properties of platinum are well marked. The thermal electromotive force of a particular piece of platinum thermoelement wire as manufactured was found to be 4 microvolts positive to a special standard at 1200° C. After degassing, by heating *in vacuo* until a discharge could no longer be obtained, the electromotive force decreased by 3 microvolts. The tensile strength of platinum is also altered by the presence of oxygen, being reduced by a variable amount. In one particular case the breaking load of a gassed wire 0.36 mm. dia. was found to be 1.12 kg., with about 3 per cent. elongation on 10 cm.; with a wire of the same size free from gas the breaking load was 1.93 kg. with an elongation of 12 per cent. The appearance of the two wires after tensile test is shown in Fig. 1. The wire free from gas is absolutely smooth and uniform in diameter, while the gassed wire is rough and exhibits a characteristic beaded appearance.

Attempts to detect gas on a polished cross-section of a casting have been made. Fig. 2 is photomicrograph of a cast bar, the whole field being of a single grain although the cellular structure could be seen in all grains. On light etching the markings were faint, and had an elongated hexagonal shape, but when etched more deeply, as shown in the photograph, the structure was clearly marked and at points on the cell borders gas holes appeared. It seems probable, in the light of present knowledge, that this phenomenon is due to the presence of oxygen, but an exact explanation of the formation of this cellular structure has not as yet been found.

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[3] Baker & Co., Research Department.
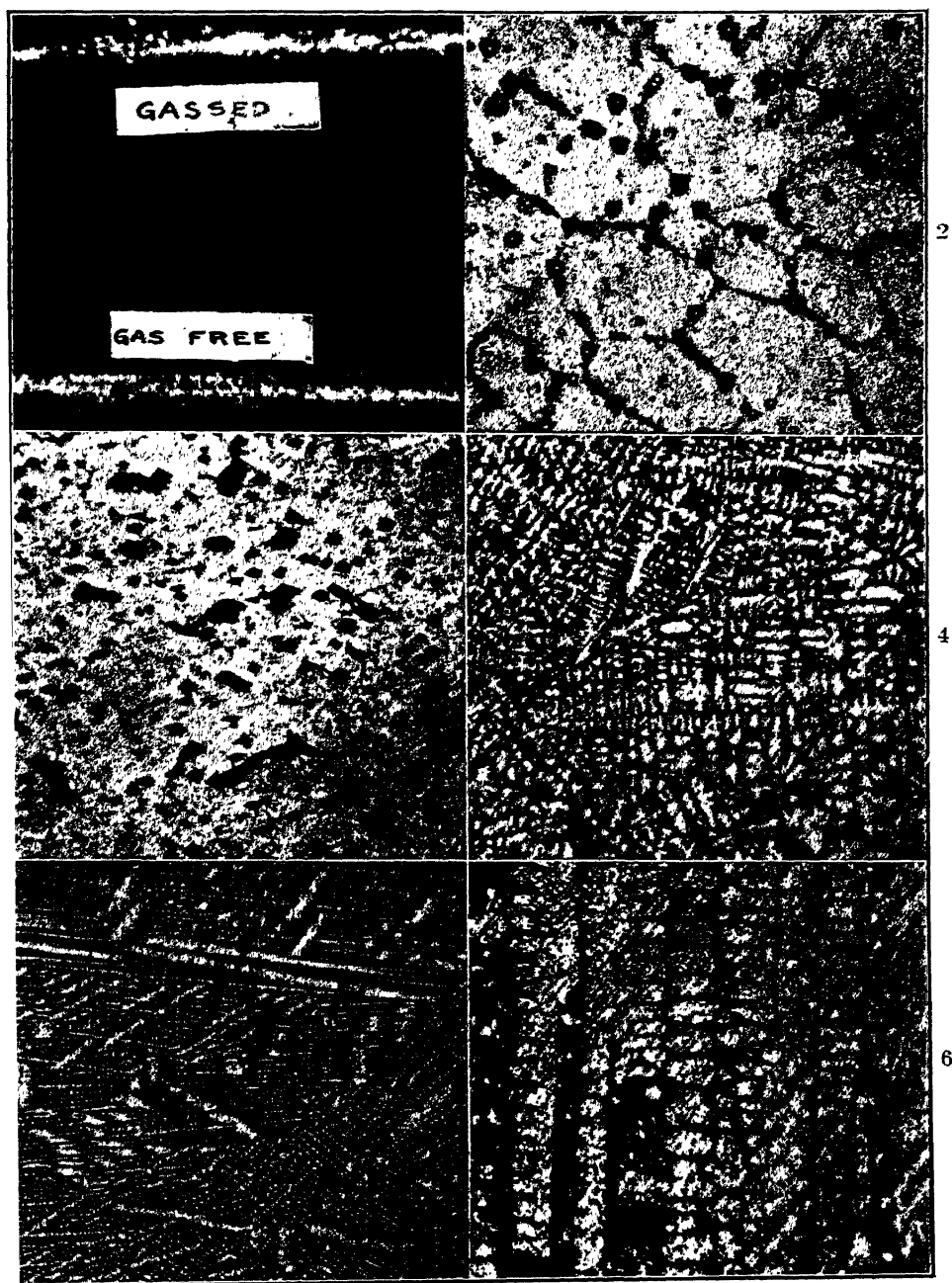
The action of hydrogen is doubtful. Kleine[4] has stated that the electrical resistance of platinum was increased by 12 per cent. by degassing, whereas Bennewitz and Gunther[5] say the absorption of hydrogen causes an increase in electrical resistance. This instance is typical of many other studies on the gas content of metal and shows that by neglecting to consider some factor the results of much laborious work are rendered valueless. Hydrogen in both platinum and palladium tends to harden and stiffen the metal. When a piece of thin foil of either metal is used as a cathode in an electrolytic cell, the absorption of hydrogen stiffens it and the resultant strains cause the foil to curl up. We are attacking the problem by melting with the atomic hydrogen torch, and our results, which are somewhat tentative, indicate that hydrogen does have a profound effect on the physical properties; for example, the thermal electromotive force 1200° C. of chemically pure platinum, such as is used for thermoelement wire, is increased by 750 microvolts against standard platinum by such treatment. This effect must be due to absorbed hydrogen, as spectrographic examination failed to reveal more than the usual faint traces of impurities. Hydrogen, of course, would not be evident on a spectrogram. Up to the time of writing no really workable piece of metal has been obtained by melting with an atomic hydrogen torch, since, on working, the buttons invariably pull apart with a peculiar crystalline fracture. This may be a characteristic effect of the presence of hydrogen, but we are not prepared to make a definite statement on this point.

In regard to rhodium and iridium, the only data available indicate that they absorb oxygen to a great degree. On melting these metals in the oxyhydrogen flame and pouring, it is no uncommon experience to find that gas rejection on solidification causes the metal to swell to twice its volume. As with platinum and palladium, melting in atomic hydrogen renders rhodium and iridium very brittle but so far very little work has been done on the effect of absorbed hydrogen.

[4] H. Kleine: Widerstandsänderungen eines Platin- und eines Eisendrahtes im Hochvakuum in Abhängigkeit von der Gasbeladung. *Ztsch. f. Physik* (1925) **33**, 391.

[5] K. Bennewitz and P. Gunther: Über den Zustand des in Platin gelösten Wasserstoffs. *Ztsch. f. phys. Chem.* (1924) **111**, 256.

FIG. 1.—PLATINUM WIRES AFTER TENSILE TEST. × 20.

FIG. 2.—OXYGEN IN PLATINUM. ETCHED IN 50 PER CENT. AQUA REGIA: × 75.

FIG. 3.—GRAPHITE IN PLATINUM. ETCHED IN 50 PER CENT. AQUA REGIA. × 75.

FIG. 4.—NORMAL STRUCTURE OF ALLOY OF PLATINUM 80 PER CENT., IRIDIUM 20 PER CENT. AS CAST. ETCHED IN CONCENTRATED AQUA REGIA. × 75.

FIG. 5.—ABNORMAL STRUCTURE OF ALLOY OF PLATINUM 80 PER CENT, IRIDIUM 20 PER CENT. AS CAST, DUE TO ABSORPTION OF CARBON. ETCHED IN CONCENTRATED AQUA REGIA. × 75.

FIG. 6.—PLATINUM MELTED IN ARSEM FURNACE, SHOWING PRESENCE OF CARBON. ETCHED IN 50 PER CENT. AQUA REGIA. × 100.

REFRACTORIES

When dealing with metals of such high melting points, the question of the refractory becomes very important. Few substances can be used at these high temperatures and these have all been tried at various times by different investigators. Details are available in papers by Wichers[6] and by Neville,[7] so that only a very brief account will be given here.

The refractory in general use is lime, first introduced by Deville and Debray in 1856. It is almost an ideal refractory for the melting of the platinum metals and can be obtained readily with sufficient purity, up to a CaO content of about 95 per cent., the balance being moisture, carbon dioxide, silica and traces of iron and magnesium. The melting point of lime is in the neighborhood of 2600° C., yet in melting large quantities of metal the surface of the crucible softens somewhat and glazes over. Under strongly reducing conditions the lime can be decomposed,[8] but under usual manufacturing conditions only spectrographic traces of calcium can be found in the finished metal. Judging from the *raies ultimes* the actual percentage of calcium is of the order of 0.0001 per cent. Even under strongly reducing conditions sufficient calcium is not absorbed to affect the physical properties of the metal to any extent, although its presence makes itself apparent in an increased thermal electromotive force. Lime also has an excellent slagging action, combining readily with any base metal oxides which are formed, and this property is occasionally used to assist the refiner.

There are one or two objections to the use of lime. It has the disagreeable property of absorbing moisture and carbon dioxide and when this has occurred the subsequent heating causes the crucible to swell and crumble and develop large cracks. This objection, of course, can be overcome by using only recently burned material. Lime powder cannot be easily bonded except by pressure. In Europe blocks of quicklime are used, but these are not readily available in the United States, and it is the more common practice to press crucibles from powder, using hydraulic pressure to force the powder into an iron frame. In this way strong crucibles can be prepared very cheaply, but they cannot be used for more than one or two melts, at the most, because of shrinkage and consequent cracking of the lime.

Refractories made of other substances, such as silica, magnesia, alumina, thoria and zirconia, are possible, and much work has been done in attempting to apply them to the melting of the platinum metals. Of these the first three are abundant and can be obtained very cheaply

[6] E. Wichers: The Preparation of Pure Platinum. *Jnl.* Amer. Chem. Soc. (1921) **43**, 1268.

[7] R. P. Neville: The Preparation of Platinum and of Platinum-Rhodium Alloy for Thermocouples. *Trans.* Amer. Electrochem. Soc. (1923) **43**, 371.

[8] E. Wichers: *Loc. cit.*

with a high degree of purity. They have, in common, one fault, which is very serious and practically removes them from consideration for crucible material—in even slightly reducing conditions, these three oxides can be reduced to metal, which is absorbed by the platinum and renders it brittle. Wichers[9] has shown, for instance, that in the presence of carbon magnesium can be absorbed up to 3 per cent. of the weight of the melt. For this reason alone these oxides cannot be used except for very small melts made with a hand torch, when every precaution is taken to keep an oxidizing atmosphere. The behavior of thoria and zirconia for use in the melting of pure platinum was determined by the U. S. Bureau of Standards some years ago and described in a paper by Neville.[10] These two substances seemed to be satisfactory, in that no reduction with consequent contamination of the melt was found, but the crucibles were somewhat fragile and showed a tendency to crack. This could be overcome, and the extended use of these oxides depends on whether they can be obtained with sufficient purity and cheapness. Up to the present, the cost is prohibitive, being more than 15 times the cost of pure lime. Unless new sources of supply are developed there seems to be little likelihood that lime will be replaced as the favored refractory for platinum melting.

We have not mentioned the use of graphite, which, with its mechanical strength, its cheapness, purity and uniformity, and above all its ability to withstand high temperatures, would seem to be almost ideal for platinum melting. There is, however, one property of carbon that is fatal to its use as a crucible—it combines readily with the platinum metals, lowering the melting point and rendering the metal very brittle. Fig. 3 is a photograph of a bar of platinum that has been melted in a graphite crucible in an induction furnace. The black specks and flakes are precipitated graphite and, though this is a photograph of only one grain, were uniformly distributed across the cross-section. The ease with which graphite is oxidized also is an obstacle to its use as a crucible.

INGOT MOLDS

The ingot molds for the platinum metals are usually made from graphite or silica, graphite being preferable because of its better chilling properties. It is generally used cold, although it may be heated to from 100° to 200° C. to remove moisture from the surface of the mold. Great care must be exercised not to overheat the mold; if it is too hot, the molten metal attacks it and forms the carbide. The absorption of the carbide greatly affects the crystal structure of the metal, as is shown by Figs. 4 and 5. The alloy in this instance was 20 per cent. iridio-platinum, which is largely used for contact material and resistance wires. Fig. 4 shows

[9] E. Wichers: *Loc. cit.*
[10] R. P. Neville: *Loc. cit.*

the normal structure of a cast bar with well-rounded dendrites, and Fig. 5 is a cross-section of a bar that was poured in a hot carbon mold and attacked the walls severely. It will be noted that the character of the dendrites is completely changed. They are small and acicular instead of the large fully rounded type of Fig. 4. This bar was very brittle and did not possess the ductility of the bar of which Fig. 4 is a cross-section. In addition to the possibility of carbide formation, it is probable that, if the melt is oxidized to any extent and the graphite is attacked, formation of carbon monoxide will result, which renders the bar somewhat unsound.

In the construction of the mold, care must be taken that the cooling rate is such that the complete elimination of gas can take place before solidification. Frequently gas is forced to the center of the bar and is trapped by freezing over of the surface, leaving a long pipe down the center. This pipe is not welded by subsequent hot working, as the surface is covered with a platinum oxide, which, although freely volatile above 900° C. cannot escape from the pipe and interferes with the weld. To some extent the gas rejection and cooling rate can be cared for by a skilfully controlled pouring rate, the metal being fed into the mold at just about the speed it solidifies.

Silica molds tend to the formation of very large grains, as their chilling effect is so much less. As a result of these large grains, much greater care is necessary in working these bars. The use of silica molds is confined to special cases; e. g., where gas solubility is high and sufficiently slow cooling is required to rid the metal of its dissolved gas.

The use of a hot top to the mold to keep the top of the bar molten, so that there is a constant feed in of metal to take care of any shrinkage, is common in many branches of metallurgical work. Such a method has often been considered for use in melting the platinum metals but up to the present no practicable means of applying it have been devised. We have to contend with the high melting point and the small size of the melts, with the consequent rapidity of solidification. It is better to trust to the skill of the melter in judging the correct rate of flow of the liquid metal into the mold. This rate, of course, varies with the temperature of the melt; the higher the temperature, the slower the rate of pour necessary.

ARC MELTING

Until the introduction of the arc furnace, the oxyhydrogen flame was the only available method of melting the platinum metals. The first arc type of furnace where heating was done by radiant heat was constructed by Siemens and Huntington but it was not until Moissan's classical work in 1892 that the full possibilities of the arc were apparent. His account of his experiments with this new furnace is a fascinating

story and it is easy to picture his dreams of the possibilities opened up by this application of electric heat. While his original purpose for the use of this furnace—the manufacture of diamonds—has not been realized, the arc furnace has attained a very important place in metallurgy. Modern furnaces differ greatly in design and capacity from Moissan's crude apparatus but to him we must give the credit of showing the way to the application of the electric arc to melting.

In the platinum industry the electric arc has not made much headway. The presence of carbon and carbon vapor causes the formation of carbides, which render the metal brittle and unworkable. In common with the arc, the Arsem type of furnace is not suitable for melting platinum metals because of the presence of carbon vapor. Fig. 6 shows the structure of platinum heated in the Arsem furnace and is typical of one of the forms in which carbon is present.

INDUCTION MELTING

It has often been said that the future of metallurgy lies in the production of gas-free ingots, and the truth of this statement is attested by the large volume of literature on the reactions between gases and metals. Gas solution is particularly important in the platinum industry and is the major source of trouble in the manufacture of articles of the platinum metals. This was fully realized by E. A. Colby,[11] who in April, 1887, filed his first patents for the design of an induction furnace providing means for both melting and pouring in a vacuum. In recent years Rohn,[12] in Germany, has based a large industry on vacuum melting and pouring by means of the induction furnace. The basic features of this furnace are that the primary consists of a water-cooled copper coil wound around the core, with the melt forming a closed secondary outside the primary winding. The power supply is low-frequency alternating current.

While this type of furnace is efficient, it is not suitable for melting the platinum metals, because of the small volume of individual melts and the necessity for having a closed ring of metal to start the furnace. The high-frequency coreless induction furnace which has been developed by Northrup is preferable to the low-frequency induction furnace and it is with this that research is being carried out by the writer. The furnace lends itself not only to melting in any chosen gaseous atmosphere, but also to melting and pouring in a vacuum. However, the practical application of this idea involves the surmounting of many difficulties.

In applying the method to platinum melting our lack of knowledge of chemistry at the temperature at which these metals melt is a stumbling

[11] E. A. Colby: U. S. Patents 428378, 428379, 428552 (May 20, 1890).
[12] W. P. J. Rohn: The Reduction of Shrinkage Cavities and Vacuum Melting. *Jnl.* Inst. Met. (1929) **42**, 203.

block.   As an instance of what may occur, note the reduction of lime by platinum when melting *in vacuo*, mentioned by Carter.[13]   The absorption of the resultant calcium by the melt affects the physical properties and may render the platinum unworkable.   This reduction has not yet been found in zirconia or thoria but their high cost prohibits general use.   The crucibles commercially available are all attacked by the molten metal and the ingots produced are invariably brittle.

The manufacture of crucibles of lime, zirconia or thoria, suitable for induction melting large quantities is as yet an unsolved problem.   As is well known, the efficiency of the high-frequency induction furnace depends on the ratio between the diameter of the melt and the diameter of the coil, and to attain maximum efficiency it is necessary to have as little thickness of insulation as possible between the coil and the crucible and, if a nonconducting crucible is used, to have it thin-walled.   Pressed lime blocks are somewhat fragile when removed from their frame and cannot be drilled to a thin wall form, and if drilled before removal from the frame, the operation of removal nearly always breaks the wall. Tamping lime around a graphite rod and heating the rod produces a fairly good surface on the inside of the crucible but the writer has found that the top of this crucible is very soft and unsuitable for any method of melting where the metal is to be poured over the top of the crucible.

A method of crucible preparation that gives greatest promise is to line a silica crucible with either zirconia or thoria and research is being carried on in this direction.   The advantages offered are a crucible of mechanical strength, a resistance to the attack of the metal and a reduction in the amount of refractory necessary.   The problem is not yet solved, a suitable binder being the bar to progress.

ATOMIC HYDROGEN FLAME

The newest tool for melting given to us by modern scientific research is the atomic hydrogen torch, by Langmuir, of the General Electric Co. This tool has shown a great usefulness and a promise for the future. There is a certain amount of hydrogen absorption but this does not seem to have a seriously detrimental effect on the metal, beyond making both platinum and palladium somewhat harder.   It is remarkable that no tungsten appears to be absorbed by the melt and there seems to be no appreciable reduction of lime.   In a particular experiment, samples of platinum sponge were melted into bars by both the oxyhydrogen and the atomic hydrogen flame and were then examined spectrographically.   In both cases the calcium content was less than 0.001 per cent., and probably less than 0.0001 per cent.   No trace of tungsten could be found in that melted in atomic hydrogen.   This part of the problem is still under

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[13] F. E. Carter: Some Notes on the Metals of the Platinum Group.   *Trans.* Amer. Electrochem. Soc. (1923) **43**, 400.

investigation, as we believe that tungsten is one of the elements that is difficult to detect by means of spectrography of the ultra violet.

WORKING

Of the six metals comprising the platinum group, only two, platinum and palladium, are easily workable. Rhodium and iridium can be worked but they require special processes and their production is still a laboratory matter. In addition, the available quantities of these two elements are somewhat limited and the uses for them as such are very few, so that it is not likely that their production will be systematized like that of platinum or palladium. The working methods are dealt with later in this paper.

Platinum and palladium are both soft and ductile metals. Their physical properties have been given by Carter,[14] so no detailed account will be given here. Of the two, platinum is the more ductile, but the difference is so slight that in working it is hardly noticeable, and the two metals receive the same treatment. A detailed account has been given in the same paper regarding the alloys of platinum and palladium but it has been found, principally by results obtained in a study of the thermal electromotive force, the electrical resistance and the microstructure, that the alloys of Pt-Cu, Pt-Au and Pd-Cu are not such simple systems as was at first supposed. Our results cannot be closely indicated here, but some information on this subject has already been published by two Swedish workers, Johansson and Linde.[15]

The methods of working the alloys are essentially the same as those of working the pure metals, with differences only in the amounts of reduction between annealings.

Platinum, palladium and most of their alloys are usually given their first reduction at a temperature above 800° C., although they can be worked cold. This process is capable of giving a rapid reduction, in sheet rolling as much as 50 per cent. reduction in thickness being obtained in one pass. Naturally, with the harder alloys such large reductions cannot be taken. Gas holes and pipes in the body of the bars are usually closed by this process but welding rarely takes place, probably, as mentioned earlier in this paper, because of the presence of a layer of platinum oxide on the

[14] F. E. Carter: The Platinum Metals and Their Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 759.

[15] C. H. Johansson and J. O. Linde: Röntgenographische Bestimmung der Atomanordnung in den Mischkristallreihen Au-Cu und Pd-Cu. *Ann. d. Physik* (1925) **78**, 439.

  Kristallstruktur, elektrischer Warmeleitfähigkeit, magnetische Suszeptibilität, Harte und Vergutungserscheinungen des Systems Au-Pt in Verbindung mit dem Zustandsdiagramm. *Ibid.* (1930) **85**, 762.

  Gitterstruktur und elektrisches Leitvermiögen der Mischkristallreihen Au-Cu, Pd-Cu und Pt-Cu. *Ibid.* (1927) **52**, 449.

walls of the cavities. The initial hot work on a wire bar is usually done under a hammer or in wire rolls.

The presence of gas in very large amounts is shown at this stage. In sheet rolling the edges of the bar burst out in a characteristic fracture and sometimes cracks form on the surfaces of the bar. In wire bars the corners fracture with irregularly shaped cracks. This type of crack cannot be confused with hardness cracks due to too severe work.

When a bar is badly piped it often splits along the pipe, and in certain cases the two halves of the bar spread in a manner similar to an alligator's jaws. This occurs most frequently with the harder alloys, the softer not showing the presence of the pipe until later stages.

In this hot working the surface of the bar is contaminated with iron, which is present principally as scale and can be easily removed by boiling vigorously in hydrochloric acid. Very little iron actually alloys with the platinum, as is shown by an experiment made with a bar of thermoelement platinum which was cast 2.5 cm. square. After the hot working was finished, the bar, now 1 cm. dia., was boiled in hydrochloric acid for its usual time. It was then cut into two sections and in one the core was drilled out, leaving as thin a shell as possible, actually about 1 mm. thick. The other half was turned down to about 2 mm. dia. Both halves were then drawn into wire and their thermal electromotive force against a standard was determined at 1200° C. Both tested +3 microvolts. As a check, the two wires were coupled and with the hot junction at 1200° C. and the cold at 0° C., no electromotive force could be found.

Cold work on sheet is carried out by 5 to 10 per cent. reduction in thickness per pass, which, together with the reduction between annealings and the annealing temperature, depends on the particular metal or alloy being worked.[16] For pure platinum the temperature for full softening is about 650° C. The addition of alloying elements raises this temperature appreciably, iridium raising it more than rhodium. For instance, 10 per cent. iridium becomes fully annealed in five minutes at 1150° C., whereas 10 per cent. rhodium requires only a temperature a little above 900° C.

Annealing of the cold-worked sheet shows, as with all metals, the presence of any blisters. The only cure for this disease is to remelt the bar. It is probable that in the platinum industry there is more trouble with blisters than in any other metal-working industry, as, apart from the affinity of the metals for gases, there are great difficulties in temperature control of the melts. Many schemes have been tried but not one has given reliable results and reliance must be placed on the sometimes fickle judgment of the melter.

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[16] F. E. Carter: The Platinum Metals and Their Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 759.

The sheet is formed to various shapes by the usual cold-forming methods, spinning, stamping, bending cold and drawing in dies, with suitable annealing. Many articles are made by welding, as platinum possesses the remarkable property of softening at a low temperature and welding if gently hammered. This property is largely used in the manufacture of electrodes for many purposes, various types of platinum assembly, contact cylinders for ammonia oxidation catalysis, etc. Where soldering is necessary, the best solder is fine gold, although a number of platinum solders are made.

A large amount of seamless tubing is made by drawing a circular blank into a cup and then drawing this on a mandrel through dies to the required diameter and wall thickness. The process is not possible with platinum alloys containing more than about 15 per cent. iridium or 20 per cent. rhodium.

Both platinum and palladium are somewhat difficult to work on a punch press or a lathe. They drag on the punches and gradually build up a layer of metal which may result in breakage of either the punch or the die. Palladium is worse than platinum in this respect. The trouble can be cured to some extent by suitable alloying, usually by the addition of iridium to platinum and ruthenium to palladium and by the choice of a suitable lubricant on the punch. In the lathe neither metal cuts cleanly, the cure being the same as for the punching difficulty.

In the manufacture of wire, after hot rolling it is cleaned and annealed, as the hot work usually finishes well below the recrystallization temperature. It is then either cold-rolled through grooved rolls or swaged, the particular operation depending on the amount of metal to be worked, although the hardness of the alloy is also a deciding factor. Some of the harder alloys always fracture on cold rolling but can be reduced quite satisfactorily by swaging. Swaging is done with 10 to 15 per cent. reductions between dies, and being a much more rapid operation than rolling is particularly suitable for large quantities. For the pure metals and softer alloys, the reduction between dies may be as much as 30 or 40 per cent., but when large quantities are being handled this is not usually done, as it is somewhat drastic treatment for the swager.

After swaging, further work is done by drawing through sapphire or tungsten carbide dies. The latter material has been found to have excellent properties for the drawing of the platinum metals. It produces a very fine surface, maintains its size well and takes less power than the sapphire dies for the same draft. It takes more power than diamond dies, and the smaller sizes of wire, for this reason, are drawn on diamond dies. The drawing is done on continuous machines with drafts of 10 per cent. between dies at the larger sizes, but as the size of the wire becomes less the draft must be reduced.

Bare drawing is done on many alloys to 0.0004 in. dia., which is about the practical limit for wire drawing. However, smaller sizes of wire can be obtained by the Wollaston process. This process consists of inserting a wire of the material to be drawn into a tube of a material of similar hardness and then drawing them down together. The jacket is afterwards dissolved in a medium that will not damage the core. By this process platinum and many of its alloys can be prepared down to 0.00005-in. dia. and gold down to 0.00001-in. diameter.

RHODIUM

For certain special applications, sheet and wire of rhodium are desirable. It has great value as an anode, remaining unattacked by electrolytes which rapidly erode other materials. As wire it is valuable as a furnace winding for resistance-heated furnaces where temperatures up to 1600° C. are to be obtained and maintained for a considerable period. The supply of the metal is too small for it to come into extensive use and the metal and the high rhodium-platinum alloys are only a laboratory product.

Rhodium cannot be melted or worked in the same manner as platinum or palladium. The melting procedure is fully described by Swanger[17] who recites the difficulties encountered when the operation is done either by the oxyhydrogen flame or in the high-frequency furnace. The writer has used approximately the same method as Swanger for working the rhodium into wire; viz., at first swaging and drawing very hot and gradually lowering the temperature as the diameter of the wire was reduced. Under this treatment the wire eventually attains the desired fibrous structure and is capable of being cold-drawn. In this way wire down to 0.004-in. dia. has been made.

Rhodium sheet is prepared by hot rolling to a thickness of about 0.030 in., at which size it becomes sufficiently ductile for cold rolling. During the cold work frequent annealing at high temperature is necessary. The annealed material hardens rapidly and by far the greatest reduction occurs on the first pass after annealing. The remaining reduction of thickness is very slow, several passes being required for each draft. Foil has been produced in sheets 10 by 24 by 0.001 in.; it is a commercial possibility if any use for it should be found.

IRIDIUM

Iridium can be worked in a way similar to the working of rhodium but with even greater difficulty; cold working is quite impossible, the material crumbling to small fragments after a very small reduction. It should be mentioned that even this limited workability is attained only

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[17] W. H. Swanger: Melting, Mechanical Working, and Some Physical Properties of Rhodium. U. S. Bur. Stds. *Jnl. of Research* (1929) **3**, 1029.

by iridium of high purity, the presence of minute amounts of other metals, including platinum metals, reducing the malleability to zero.

RUTHENIUM AND OSMIUM

Ruthenium and osmium have never been worked. These two metals are of different type of lattice structure from the remaining metals of the group, being hexagonal close-packed, while the others are all face-centered cubic lattice. This is probably the reason for their hardness and their tremendous hardening power when alloyed with the other metals. For instance, 15 per cent. ruthenium or 10 per cent. osmium have the same hardening effect on platinum as 20 to 25 per cent. iridium.

DISCUSSION

(Sam Tour presiding)

L. JORDAN, Washington, D. C.—What was the nature of the refractory upon which the platinum metal was supported during the melting in the atomic hydrogen flame? I judge from what was said later in the paper that it was lime and I wonder about the purity of that material. Some of our experience at the Bureau of Standards has indicated, as Mr. Sivil also points out later in the paper, that certain of the elements, particularly some of the nonmetallic impurities, are rather difficult to detect either qualitatively or quantitatively in spectrographic analysis, and I wonder whether there is not still a possibility that some nonmetallic impurity was the cause of the very great increase in thermal electromotive force of the platinum melted in the atomic hydrogen flame.

The peculiar crystalline fracture of the metal melted in the atomic hydrogen flame, which apparently interfered with its workability, recalls the experience of W. H. Swanger at the Bureau of Standards in working metallic rhodium. A fracture that I judge was rather similar to the one Mr. Sivil mentioned completely prevented working of rhodium, when it had been melted in vacuum. There was absolutely no hydrogen present and it is reasonably certain that the rhodium was still very pure metal. The nonworkability was attributed entirely to grain size. The same material prepared under conditions permitting more rapid cooling could be forged and swaged readily.

Mr. Sivil mentions that control of gas evolution from platinum may be accomplished by proper construction of the mold and skillful control of the pouring rate. An advantage of the high-frequency induction furnace in the melting of platinum metals is that by its use it is possible to cool the metal to the freezing point, thus allowing the evolution of a large portion of the dissolved gases, then remelt, repeat this cycle several times, if necessary, and finally pour the metal with much less control of the rate of pouring or of freezing in the mold and still eliminate the undesirable effects of gas evolution.

Since the published reports by Wichers and Neville dealing with refractories for melting platinum, there has been further work done at the Bureau of Standards on special refractories for such use. Swanger and Caldwell have found that beryllium oxide has very promising possibilities. Here I am speaking of small-scale use in research work, since obviously the possibility of using beryllium oxide commercially must take into consideration the relatively high cost of the material, to which Mr. Sivil referred. Beryllium oxide apparently is more stable at temperatures of from 1800° to 2000° C. than magnesium oxide or calcium oxide.

C. S. Sivil (written discussion).—I wish to thank Dr. Jordan for the suggestion of the use of beryllium oxide as a refractory. While the price of rarer refractories may seem prohibitive, they may be adopted for use in special cases, if not generally, provided that they offer sufficient advantages over lime. So far, no refractory has been found that is as suitable as lime for general melting purposes, but it has many failings, and any refractory with the good properties of lime and without its failings will be welcomed by the platinum industry.

The refractory used when melting with the atomic hydrogen flame was the usual stock lime. This material as it comes from the kiln has as impurities: MgO, 0.5 per cent.; SiO_2, 0.75 per cent.; Fe_2O_3 and Al_2O_3 together, 0.37 per cent. The prepared crucibles have been found to contain, in addition, 0.5 to 0.8 per cent. moisture and 0.2 to 0.5 per cent. CO_2. The other impurities that might be present, the sulfate or phosphate of calcium, have not been detected in the lime. This result clearly reveals the need for quantitative data on the effect of small quantities of impurities and on the effect of gases on the physical properties of platinum.

The nonworkability of the metal melted in the atomic hydrogen flame is due no doubt to the grain size of the metal, as Dr. Jordan suggests, but this is not determined by the cooling rate alone. Melts made with the oxyhydrogen torch under similar crucible and cooling conditions work excellently. The effect of small percentages of impurities, which might have been reduced by the atomic hydrogen, and in solidification have segregated at the grain boundaries, is apparently ruled out by the spectrographic analysis. It appears, therefore, in the light of our present somewhat meager information, that hydrogen when alloyed with the platinum metals can exert a profound influence on the crystal structure. Much more thorough investigation will be necessary before any definite statement can be made.

E. M. Wise, Bayonne, N. J.—I have melted a good many of these alloys myself and have encountered many of the difficulties that Mr. Sivil so ably describes. The skill of the melter and the development of a proper technique are as important in handling these metals as in any that I know of. The conditions necessary to secure sound ingots are not simple. The usual scheme available for handling most other metals is to melt them and let the oxygen content wander around to whatever value it may attain and then to add a little deoxidizer at the end of the melt. With platinum, in most cases, it is vitally necessary to maintain high purity, consequently the use of deoxidizers is usually precluded, not only for this reason, but because appreciable quantities make the metal brittle, so the only thing available is to control the flame conditions during melting to obtain the proper pitch, or use such cooling conditions as may result in the evolution of most of the detrimental gas during solidification. The latter scheme is not altogether simple. The working of rhodium and the more difficult metals is really an art at present.

Effect of Certain Alloying Elements on Structure and Hardness of Aluminum Bronze*

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For the past century, the so-called aluminum bronzes have been assuming a role of ever-increasing importance in the metallurgical field. The last quarter of that century has marked many efforts to find alloying elements that would alleviate some of the undesirable qualities of the aluminum bronzes—for example, the heterogeneity of the alpha solid solution and the extreme hardness of the beta. Much of this work, however, has been rather haphazard—compositions and heat treatment are usually so much at variance as to make comparison impossible.

It is the object of this research to study the effect of certain percentages of common alloying elements on aluminum bronzes of analogous compositions and heat treatments. It is hoped that the material gathered here will at least serve as a basis for further systematic study.

Material and Procedure

All of the alloys included in this investigation were cast in green sand at the Wright Field foundry. The plan included the study of alloys with 8, 10 and 12 per cent. of aluminum, each with 1 and 5 per cent. of the special alloying elements. This totaled six different alloys with each element, or 30 alloys in all, since five elements have been studied so far. These are nickel, iron, manganese, cobalt and silicon. Since special hardeners had to be made and some of these alloys fused only with great difficulty, the chemical analyses were somewhat erratic, as shown in Table 1. Grain-size measurements are given in Table 2 and hardness in Table 3.

TABLE 1.—*Composition of the Aluminum Bronzes*

Aluminum, Per Cent.		Copper, Per Cent.		Alloying Element, Per Cent.	
Desired	Present	Desired	Present	Desired	Present
8.00	8.43	92.00	91.57		
10.00	10.06	90.00	89.94		
12.00	11.82	88.00	88.18		
				IRON	
8.00	8.05	91.00	91.05	1.00	0.90
8.00	8.10	87.00	86.91	5.00	5.00
10.00	.10.13	89.00	88.80	1.00	1.07
10.00	9.96	85.00	84.90	5.00	5.10
12.00	11.90	87.00	87.08	1.00	1.01
12.00	12.02	83.00	83.18	5.00	4.80
				NICKEL	
8.00	. . . . .	91.00	. . . . .	1.00	
8.00	8.12	87.00	86.66	5.00	5.23
10.00	10.04	89.00	88.86	1.00	1.10
10.00	10.17	85.00	84.60	5.00	5.23
12.00	12.14	87.00	86.80	1.00	1.06
12.00	12.26	83.00	82.56	5.00	5.18
				MANGANESE	
8.00	8.27	91.00	90.75	1.00	0.91
8.00	7.98	87.00	86.60	5.00	4.94
10.00	10.24	89.00	88.67	1.00	1.02
10.00	9.92	85.00	84.44	5.00	5.13
12.00	11.80	87.00	87.10	1.00	1.01
12.00	12.02	83.00	82.55	5.00	4.99
				COBALT	
8.00	7.75	91.00	91.03	1.00	1.22
8.00	6.83	87.00	87.71	5.00	5.46
10.00	9.82	89.00	88.94	1.00	1.24
10.00	9.06	85.00	84.88	5.00	6.06
12.00	11.82	87.00	86.61	1.00	1.57
12.00	10.82	83.00	85.79	5.00	3.39
				SILICON	
8.00	8.22	91.00	90.87	1.00	0.91
8.00	8.54	87.00	86.75	5.00	4.71
10.00	9.90	89.00	89.10	1.00	0.91
10.00	9.96	85.00	84.95	5.00	5.01
12.00	12.80	87.00	86.12	1.00	1.05
12.00	12.30	83.00	83.30	5.00	4.43

TABLE 2.—*Grain Sizes of Aluminum Bronzes*

Composition		Number of Grains per Square Millimeter				
Al, Per Cent.	Alloy, Per Cent.	As Cast	Annealed	Quenched	Temp. 400° C.	Temp. 650° C
8	. . . . . .	a	0.95	1.25	0.95	0.75
	1 Fe	0.32	0.26	0.30	a	a
	1 Ni	0.10	0.06	0.28	0.12	0.08
	1 Mn	57.00	74.50	43.00	a	62.50
	1 Co	b	b	b	b, c	b, c
	1 Si	64.00	58.40	53.00	30.10	a
	5 Fe	83.00	111.00	109.00	107.00	128.00
	5 Ni	0.08	0.10	0.06	0.06	0.03
	5 Mn	94.550	19.90	76.00	30.60	20.40
	5 Co	0.14	0.14	0.11	0.47	0.43
	5 Si	a	1.40	1.10	1.00	0.95
10	. . . . . .	0.16	0.26	0.14	0.15	0.75
	1 Fe	0.21	a	0.29	0.19	0.14
	1 Ni	0.06	0.14	0.14	0.10	0.10
	1 Mn	3.90	39.00	0.20	1.00	0.40
	1 Co	60.00	57.50	38.50	35.50	61.00
	1 Si	0.20ᶜ	b	b	0.20ᶜ	0.26ᶜ
	5 Fe	166.00	77.00	57.00	55.00	63.00
	5 Ni	a	a	a	a	a
	5 Mn	13.00	1.10	5.20	4.30	0.06
	5 Co	b	0.07	b	b	b
	5 Si	92.00	a	0.20	74.00	40.00
12	. . . . . .	0.26	0.95	0.25	0.25	a
	1 Fe	0.18	0.21	0.65	0.68	0.11
	1 Ni	0.26	0.08	0.20	0.10	0.16
	1 Mn	1.80	3.70	1.60	a	a
	1 Co	0.36	0.34	a	0.70	0.90
	1 Si	0.20ᶜ	a	a	0.32	0.42
	5 Fe	13.00	a	9.60	11.30	a
	5 Ni	a	0.96	2.00	5.00	1.30
	5 Mn	9.00	6.00	4.60	8.40	8.80
	5 Co	a	a	100.00	98.00	a
	5 Si	a	a	0.20	0.34	a

ᵃ Grain boundaries too indefinite, or not apparent. ᵇ Grains too large to count.
ᶜ Small grains in large ones.

TABLE 3.—*Rockwell and Brinell Hardness Numbers of Aluminum Bronzes*

Composition		As Cast		Annealed		Quenched		Temp. 400° C.		Temp. 650° C.	
Al, Per Cent.	Alloy, Per Cent.	R	B	R	B	R	B	R	B	R	B
	......	40	....	16	....	13	....	20	....	19	
	1 Fe	37	66	24	55	16	54	22	60	30	63
	1 Ni	22	60	2	48	10	50	8	48	9	54
	1 Mn	49	77	38	65	44	72	44	73	36	66
	1 Co	12	62ᵃ	42	75	57	99ᵃ	54	96ᵃ	57	104ᵃ
8	1 Si	70	104	58	87	84	130	87	130	61	87
	5 Fe	72	113ᵇ	67	98ᵇ	61	97ᵇ	64	94ᵇ	67	96ᵇ
	5 Ni	42	70	73	102	73	115	75	111	73	109
	5 Mn	67	100ᵃ	62	95ᵃ	73	112ᵃ	87	142ᵃ	72	111ᵃ
	5 Co	87	166ᵃ	75	129ᵃ	75	131ᵃ	76	133ᵃ	75	133ᵃ
	5 Si	119	....	119	....	116	....	122	....	118	
	......	70	....	76	....	95	....	79	....	80	
	1 Fe	102	195ᵃ	84	138ᵃ	100	190ᵃ	80	128ᵃ	90	190ᵃ
	1 Ni	76	122	82	124	86	134	93	200ᵈ	72	107
	1 Mn	83	133ᵃ	92	150ᵃ	106	244ᵃ	92	156ᵃ	109	270ᵃ
	1 Co	93	178ᵃ	70	120ᵃ	76	128ᵃ	81	143ᵃ	92	178ᵃ
10	1 Si	104	202ᵇ	101	196ᵇ	111	232ᵇ	112	248ᵇ	102	190ᵇ
	5 Fe	80	153ᵇ	86	143ᵃ	94	175ᵃ	100	190ᵃ	87	153ᵃ
	5 Mn	96	172ᵃ	95	167ᵃ	104	209ᵃ	113	270ᵃ	96	175ᵃ
	5 Co	83	146ᵃ	75	134ᵃ	76	135ᵃ	76	137ᵃ	77	143ᵃ
	5 Si		....	123							
	5 Ni	88	134	74	112	87	137	84	131	82	130
	......	100	....	108	....	92	....	102	....	104	
	1 Fe	101	191ᵃ	110	273ᵃ	102	190ᵃ	109	248ᵃ	112	266ᵃ
	1 Ni	103	232ᵈ	109	325ᵈ	93	204ᵈ	103	242ᵈ	95	214ᵈ
	1 Mn	107	222ᶜ	113	240ᶜ	100	194ᶜ	106	210ᶜ	110	230ᶜ
	1 Co	103	238ᵃ	105	260ᵃ	105	278ᵃ	112	286ᵃ	105	262ᵃ
12	1 Si	115	326ᵃ	115	354ᵃ	115	326ᵃ	120	....	116	260ᵃ
	5 Fe	100	219ᵃ	112	273ᵃ	105	223ᵈ	109	259ᵃ	110	259ᵃ
	5 Ni	107	265ᵈ	104	263ᵈ	105	....	114		102	255ᵈ
	5 Mn	105	224ᶜ	108	280ᶜ	86	190ᶜ	102	212ᶜ	106	264ᶜ
	5 Co	92	175ᵃ	87	170ᵃ	103	230ᵃ	106	260ᵃ	91	182ᵃ
	5 Si	118	....	122							

ᵃ Brinell, 1500 kg.   ᵇ Brinell, 1000 kg.   ᶜ Brinell, 2000 kg.   ᵈ Brinell, 3000 kg.
All others, made with Brinell, 500 kg.   Rockwell tests made with $\frac{1}{16}$-in. ball, 100 kg., B scale.

Two molds of standard TB-2B[1] test bars were cast from each melt. These bars were cut into pieces about one inch long, and the pieces were given the following heat treatments:

1. One piece of each melt was retained to be examined as cast.

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[1] Standard Air Corps test-bar pattern for bronze.

2. All the rest of the pieces were annealed at 875° C. for 16 hr. and furnace-cooled. One piece of each melt was kept to be examined as annealed.

3. The rest of the pieces were quenched in cold water at 5° C., after heating 1 hr. at 750° C. One piece of each melt was kept to be examined in the quenched condition.

4. One piece of each melt after quenching was tempered for 1 hr. at 400° C. and furnace-cooled.

5. One piece of each melt after quenching was tempered for 1 hr. at 650° C. and furnace-cooled.

These pieces were used as metallographic specimens, and were prepared for microscopic examination in the usual way. The etchant for the alloys with 8 and 10 per cent. aluminum was a 10 per cent. aqueous solution of ammonium persulfate. A solution of four parts of a $\frac{1}{12}$ aqueous solution of ferric chloride and one part of concentrated hydrochloric acid was used for etching the alloys with 12 per cent. aluminum. These reagents are the ones recommended by Stockdale.[2]

For the determination of grain size, the method of Jeffries and Archer[3] was used. As is characteristic of the aluminum bronzes, the grains were generally either heterogeneous or excessively large, therefore these grain-size measurements are not accurate, nor are they to be taken as empirical averages. These results will suffice to show, however, the trends of grain size.

Rockwell hardness tests (B scale, 100 kg.) and Brinell hardness tests were made, wherever possible. By means of the Rockwell apparatus it was possible to detect variations in hardness in the same specimen.

MICROSTRUCTURES

The equilibrium diagram of the copper-rich copper-aluminum alloys according to Stockdale is shown in Fig. 1. As a convenient basis for comparison the structures encountered in this investigation will be discussed in their relationship to this diagram.

The photomicrographs included in this paper were selected from about 500 made during the research. Because of space limitations many of importance were omitted. They are grouped according to aluminum contents and heat treatment. Figs. 2 to 13 show the cast structures of the alloys with 8 and 10 per cent. aluminum. Fig. 2 represents the structure of the alloy with 8 per cent. aluminum and 92 per cent. copper,

[2] D. Stockdale: The Copper-Rich Aluminum-copper Alloys. *Jnl.* Inst. Met. (1922) **28**, 273.

[3] Z. Jeffries and R. S. Archer: The Science of Metals. New York. 1924. McGraw-Hill Book Co.

with no alloying elements; also, the normal cast structure of alpha plus eutectoid.   A study of these photomicrographs shows that cobalt restricts the formation of eutectoid, and silicon and manganese promote its formation.   Five per cent. silicon changes the eutectoid beyond the point of recognition (Fig. 7) and only on quenching is there any resemblance at all to the typical eutectoid (Fig. 36).   Where the photomicrograph of some alloying element has been omitted, it was because not enough
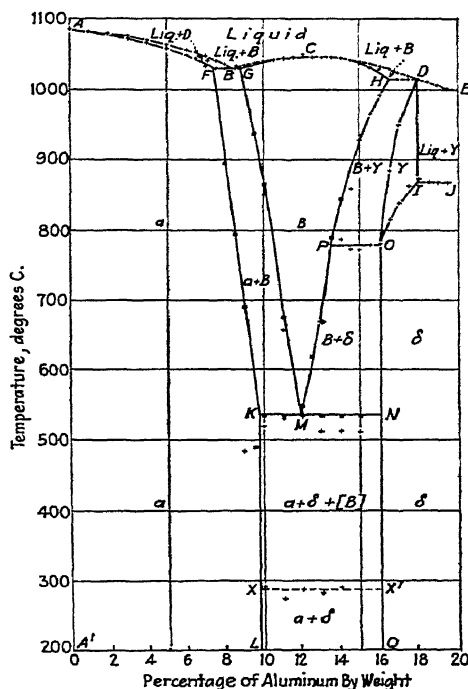
FIG. 1.—EQUILIBRIUM DIAGRAM OF COPPER-RICH COPPER-ALUMINUM ALLOYS (STOCK-DALE).

change in structure was noticed to warrant its inclusion.   Thus iron and nickel exert little influence on the cast structure of the bronze with 8 per cent. aluminum.

Fig. 8 shows the cast structure of the 10 per cent. aluminum, 90 per cent. copper alloy.   It consists of alpha plus eutectoid.   Cobalt and silicon in 1 per cent. additions promote the formation of the eutectoid, as does 5 per cent. nickel.   In 5 per cent. additions, however, cobalt and silicon suppress the eutectoid completely.

Figs. 14 to 25 show the structures of the alloys with 12 per cent. aluminum as cast and annealed.   Fig. 14 represents the characteristic eutectoid plus excess alpha structure of the 10 per cent. aluminum,
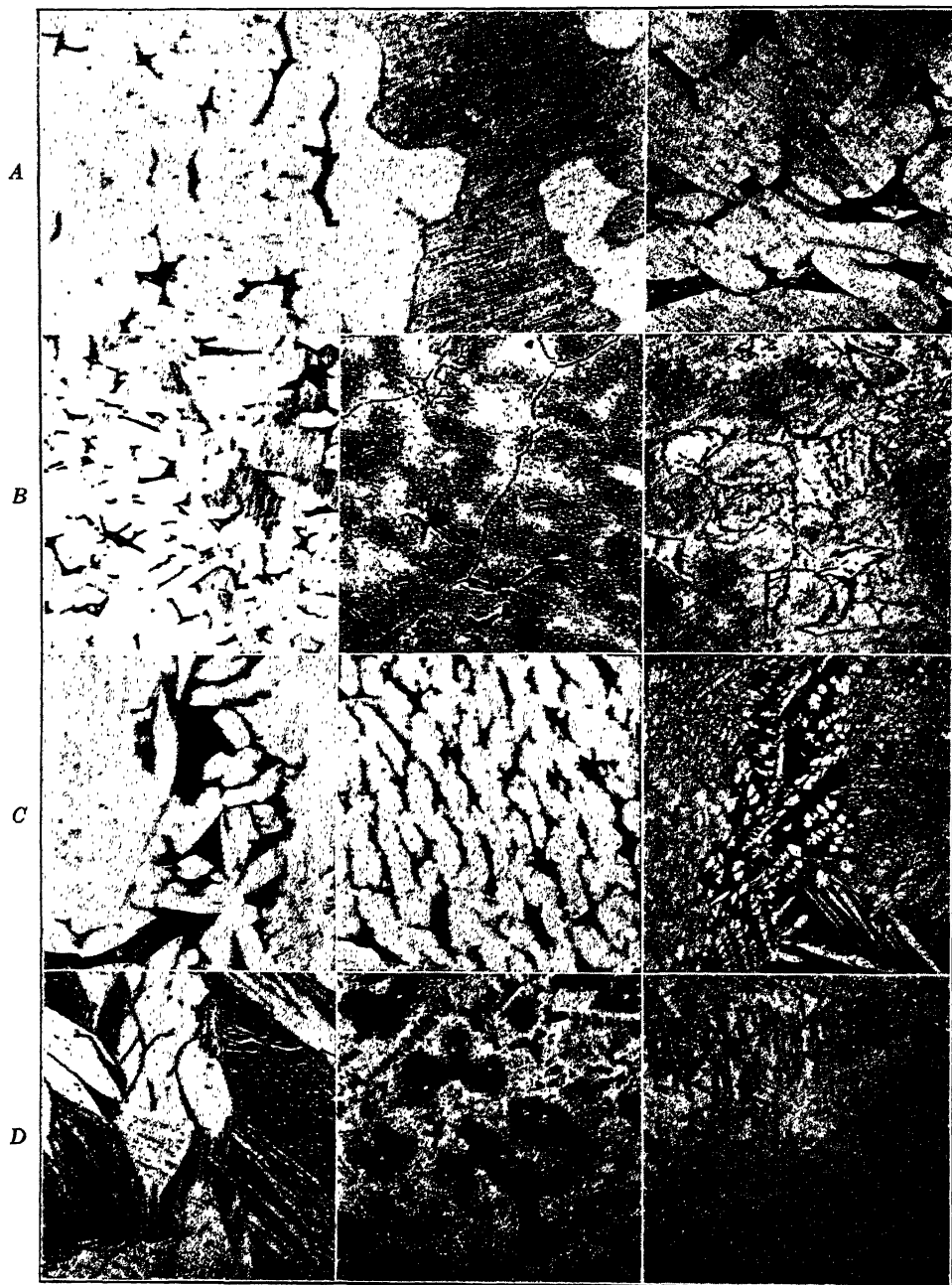
FIGS. 2–13.—CAPTIONS ON OPPOSITE PAGE.
A = Figs. 2–4.   B = Figs. 5–7.   C = Figs. 8–10.   D = Figs. 11–13.

90 per cent. copper alloy. One per cent. silicon produces much more alpha, and the same is true of 5 per cent. cobalt. Manganese effects a partial retention of beta. Five per cent. silicon produces a structure that slightly resembles beta.

Fig. 19 shows the annealed structure of the 12 per cent. aluminum, 88 per cent. copper alloy. It consists of alpha plus delta plus eutectoid. One per cent. silicon results in alpha plus eutectoid, while 5 per cent. silicon apparently produces a modified form of beta. The addition of cobalt results in a structure of alpha plus eutectoid plus a very small amount of delta. Manganese causes the eutectoid grains to decompose into practically all beta.

Nickel has the effect of decomposing the eutectoid partly into beta and some alpha. Iron results in the resolution of part of the eutectoid into alpha plus delta plus eutectoid.

Figs. 26–37 picture the structure of the alloys with 8 per cent. aluminum as annealed and quenched. Fig. 26 shows the typical twinned alpha of the 8 per cent. aluminum, 92 per cent. copper alloy as annealed. One per cent. iron results in a structure of alpha with no twins; 5 per cent. iron decreases the grain size enormously and introduces a black constituent. One per cent. silicon causes the alpha to twin excessively and results in the formation of an appreciable amount of eutectoid, but 5 per cent. of silicon produces a curiously striated form of alpha with a light yellow

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FIGS. 2–13.—CAST STRUCTURES OF ALLOYS WITH 8 AND 10 PER CENT. ALUMINUM.

FIG. 2.—AL, 8; CU, 92 PER CENT.   × 100.
Normal alpha plus eutectoid structure.

FIG. 3.—AL, 8; CO, 1 PER CENT.   × 100.
Structure all alpha, heavily mottled.

FIG. 4.—AL, 8; SI, 1 PER CENT.   × 100.
Twinned alpha plus much more eutectoid than is normally formed.

FIG. 5.—AL, 8; MN, 1 PER CENT.   × 50.
Axial alpha grains plus eutectoid.

FIG. 6.—AL, 8; CO, 5 PER CENT.   × 100.
Alpha grains, mottled, with cobalt at grain boundaries and as blue cuneiform constituent.

FIG. 7.—AL, 8; SI, 5 PER CENT.   × 100.
Alpha plus very light matrix with traces of eutectoid.

FIG. 8.—AL, 10; CU, 90 PER CENT.   × 100.
Normal cast structure of alpha grains with eutectoid at grain boundaries.

FIG. 9.—AL, 10; CO, 1 PER CENT.   × 100.
Alpha plus much eutectoid. Alpha not quite characteristic.

FIG. 10.—AL, 10; SI, 1 PER CENT.   × 100.
Large grains with excess alpha; eutectoid at grain boundaries.

FIG. 11.—AL, 10; NI, 5 PER CENT.   × 500.
Axial grains of alpha plus eutectoid.

FIG. 12.—AL, 10; CO, 5 PER CENT.   × 100.
Matrix evidently modified alpha. Blue constituent in grains and at boundaries due to cobalt.

FIG. 13.—AL, 10; SI, 5 PER CENT.   × 500.
Needlelike structure (beta?) precipitating from alpha grains. Free silicon present.
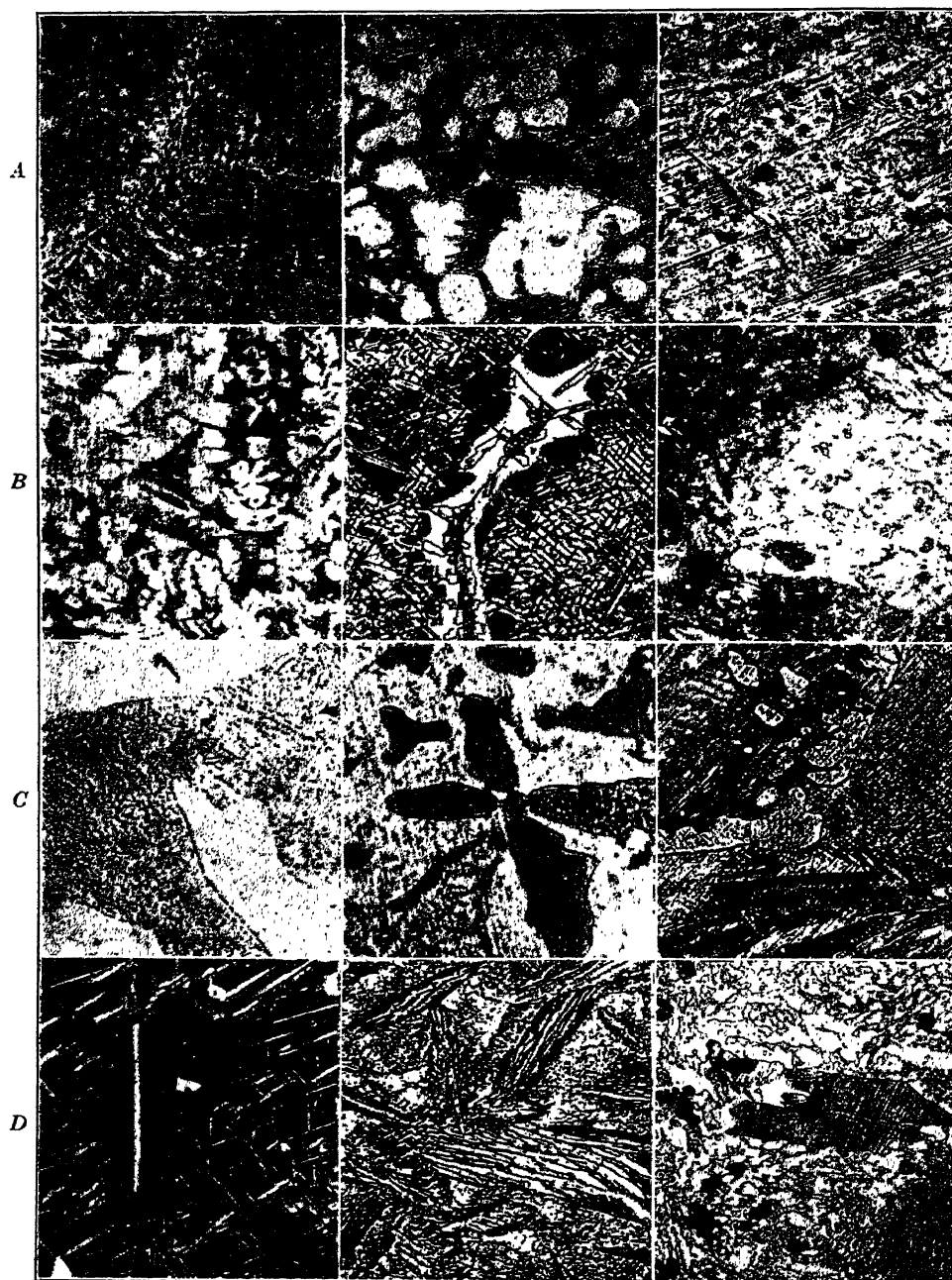
FIGS. 14–25.—CAPTIONS ON OPPOSITE PAGE.
A = Figs. 14–16. B = Figs. 17–19. C = Figs. 20–22. D = Figs. 23–25.

constituent taking the place of the eutectoid. Much free silicon can be seen. Cobalt produces an all-alpha structure in both 1 and 5 per cent. additions—5 per cent. merely causes the formation of more of the special cobalt constituent. Nickel produces a mottled form of alpha plus laminated eutectoid. Manganese effects the formation of more eutectoid than usual. There are small particles of the manganese constituent to be found in the alpha grains.

Quenching produces a structure of highly twinned alpha plus acicular beta in the alloy with 1 per cent. silicon, as would be expected from the annealed structure of this alloy. Five per cent. silicon results in a structure of alpha plus a constituent somewhat resembling eutectoid. Five per cent. manganese changes the structure to alpha plus much beta.

Figs. 38 to 49 show the structure of the alloys with 10 per cent. aluminum, as annealed and as quenched. Fig. 38 shows the normal structure of the aluminum bronze with 10 per cent. aluminum as annealed. Alpha and eutectoid are present. One per cent. cobalt causes a reduction in grain size, twinning in the alpha grains, and the formation of much less eutectoid. The eutectoid is completely suppressed and the alpha grains are twinned and heavily mottled by the blue cobalt constituent when 5 per cent. cobalt is present. One per cent. manganese shows a structure of alpha plus partly decomposed eutectoid. Five per cent. manganese decomposes the eutectoid somewhat more and introduces a special man-

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FIGS. 14–25.—ALLOYS WITH 12 PER CENT. ALUMINUM AS CAST AND ANNEALED.

FIG. 14.—AL, 12 PER CENT.; NO ALLOYING ELEMENT. × 100. AS CAST.
Large grains of eutectoid with slight amount of excess alpha at boundaries

FIG. 15.—AL, 12; SI, 1 PER CENT. × 100. AS CAST.
Alpha plus eutectoid plus blue particles of free silicon.

FIG. 16.—AL, 12; MN, 5 PER CENT. × 100. AS CAST.
Large grains of eutectoid evidently breaking down into beta plus alpha. Dark clusters of a constituent due to the manganese.

FIG. 17.—AL, 12; CO, 5 PER CENT. × 100. AS CAST.
Alpha plus eutectoid plus cobalt constituent.

FIG. 18.—AL, 12; SI, 5 PER CENT. × 500. AS CAST.
Needlelike structure (modified beta?) plus free silicon.

FIG. 19.—AL, 12 PER CENT.; NO ALLOYING ELEMENT. × 500.
Alpha plus delta plus eutectoid. Annealed.

FIG. 20.—AL, 12; SI, 1 PER CENT. ANNEALED. × 500.
Alpha plus eutectoid plus tiny particles of free silicon.

FIG. 21.—AL, 12; CO, 5 PER CENT. ANNEALED. × 500.
Alpha, somewhat modified, plus eutectoid plus Co constituent. Black constituent around grains is apparently delta.

FIG. 22.—AL, 12; MN, 5 PER CENT. ANNEALED. × 500.
Eutectoid almost completely decomposed into beta. Manganese particles have coalesced at grain boundaries.

FIG. 23.—AL, 12; SI, 5 PER CENT. ANNEALED. × 500.
Modified form of beta, with free silicon.

FIG. 24.—AL, 12; NI, 5 PER CENT. ANNEALED. × 500.
Probably beta, plus some eutectoid. No evidence of nickel.

FIG. 25.—AL, 12; FE, 5 PER CENT. ANNEALED. × 500.
Eutectoid plus alpha plus delta. Nodular iron constituent.
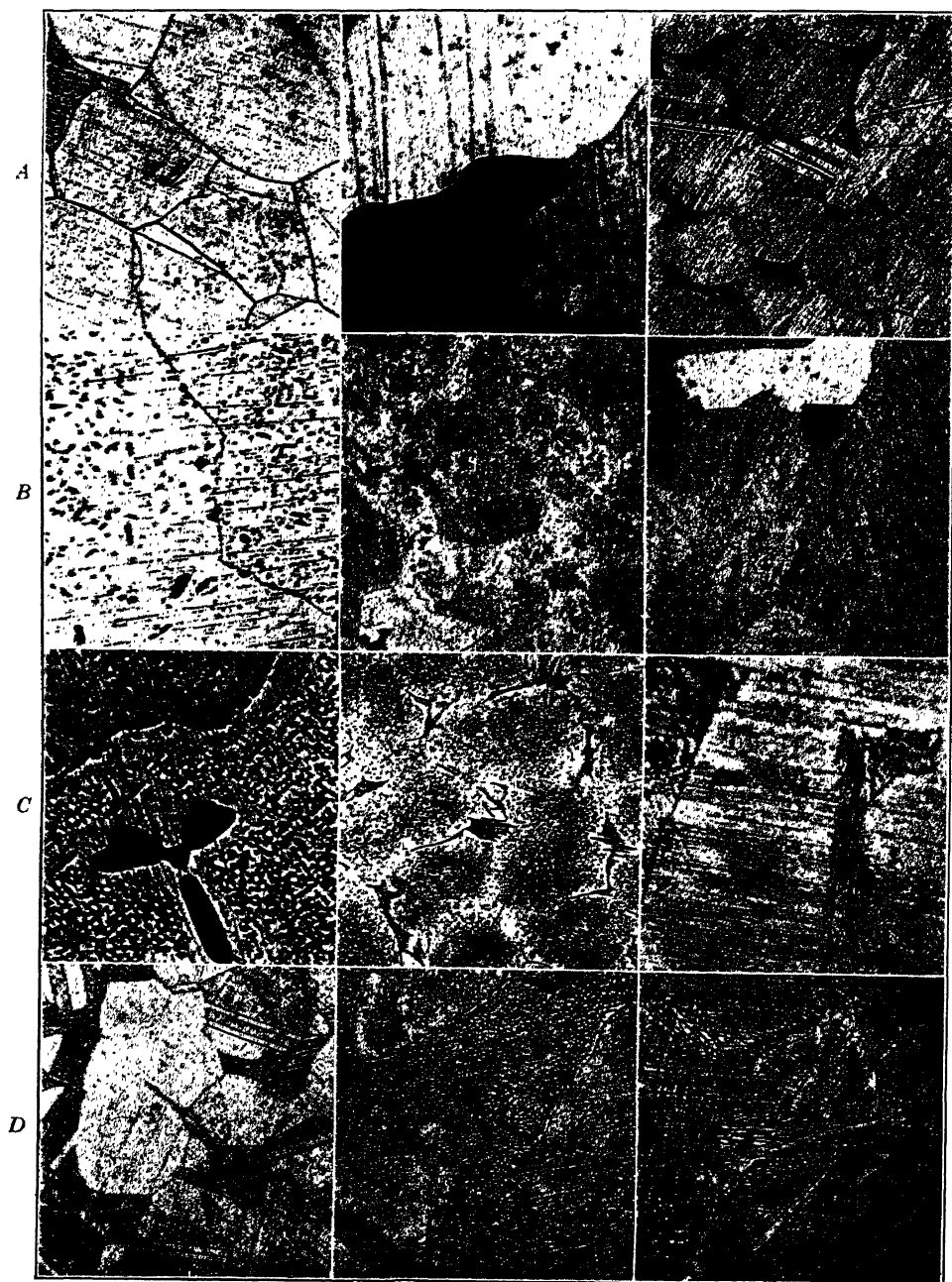
FIGS. 26–37.—CAPTIONS ON OPPOSITE PAGE.
A = Figs. 26–28.   B = Figs. 29–31.   C = Figs. 32–34.   D = Figs. 35–37.

ganese constituent in the alpha grains. Nickel produces a structure of alpha plus eutectoid almost identical with that of the normal aluminum bronze (Fig. 38), except for the rod-shaped nickel constituent in the alpha grains. Silicon produces a light structure with small regular needles, possibly a modified form of beta. Fig. 45 shows the alpha plus beta structure of the normal 10 per cent. aluminum alloy as quenched. Manganese produces large grains of beta with alpha as a tiny constituent scattered throughout the specimen. Silicon, on the other hand, produces all alpha, with free silicon present. One per cent. iron produces alpha plus beta, with a tiny constituent present in the alpha grains. Five per cent. iron introduces twins in the alpha and a nodular iron constituent in both the alpha and the beta.

Figs. 50–58 include the structures of the alloys with 8 per cent. aluminum, tempered at 400° C. and at 650° C. Fig. 50 is the normal structure as drawn at 400° C. It consists of large grains of twinned alpha plus a very small amount of beta. One per cent. silicon increases the amount of beta enormously, but when tempered at 650° C. the beta degenerates to a hard blue network constituent. One per cent. cobalt results in a structure of exceedingly fine-grained, twinned alpha, heavily mottled. Nickel produces large soft grains of alpha with a dot constituent in some of the grains, when tempered at 650° C. Manganese, when tempered at 400° C. produces alpha grains and shows the decom-

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FIGS. 26–37.—STRUCTURES OF ALLOYS WITH 8 PER CENT. ALUMINUM, ANNEALED AND QUENCHED.

FIG. 26.—AL, 8 PER CENT; NO ALLOYING ELEMENT. ANNEALED. × 100.
Normal twinned alpha. Very large grains.

FIG. 27.—AL, 8; FE, 1 PER CENT. ANNEALED. × 50.
Large grains of alpha, no twins.

FIG. 28.—AL, 8; SI, 1 PER CENT. ANNEALED. × 100.
Small twinned grains of alpha plus some eutectoid.

FIG. 29.—AL, 8; CO, 1 PER CENT. ANNEALED. × 500.
Large grains of alpha with blue cobalt constituent in grains and at boundaries.

FIG. 30.—AL, 8; FE, 5 PER CENT. ANNEALED. × 100.
Very small grains of alpha; nodular constituent of iron.

FIG. 31.—AL, 8; SI, 5 PER CENT. ANNEALED. × 500.
Alpha shows curious striations. No eutectoid. Free silicon present.

FIG. 32.—AL, 8; CO, 5 PER CENT. ANNEALED. × 500.
Alpha grains with excess cobalt constituent precipitated in grains and at boundaries.

FIG. 33.—AL, 8; NI, 5 PER CENT. ANNEALED. × 500.
Alpha mottled plus eutectoid.

FIG. 34.—AL, 8; MN, 5 PER CENT. ANNEALED. × 500.
Long axial grains of alpha plus eutectoid. Particles of blue manganese constituent in alpha grains.

FIG. 35.—AL, 8; SI, 1 PER CENT. QUENCHED. × 100.
Twinned alpha plus beta.

FIG. 36.—AL, 8; SI, 5 PER CENT. QUENCHED. × 100.
Grains of alpha plus grains somewhat resembling eutectoid.

FIG. 37.—AL, 8; MN, 5 PER CENT. QUENCHED. × 500.
Alpha plus beta plus some ree manganese constituent.
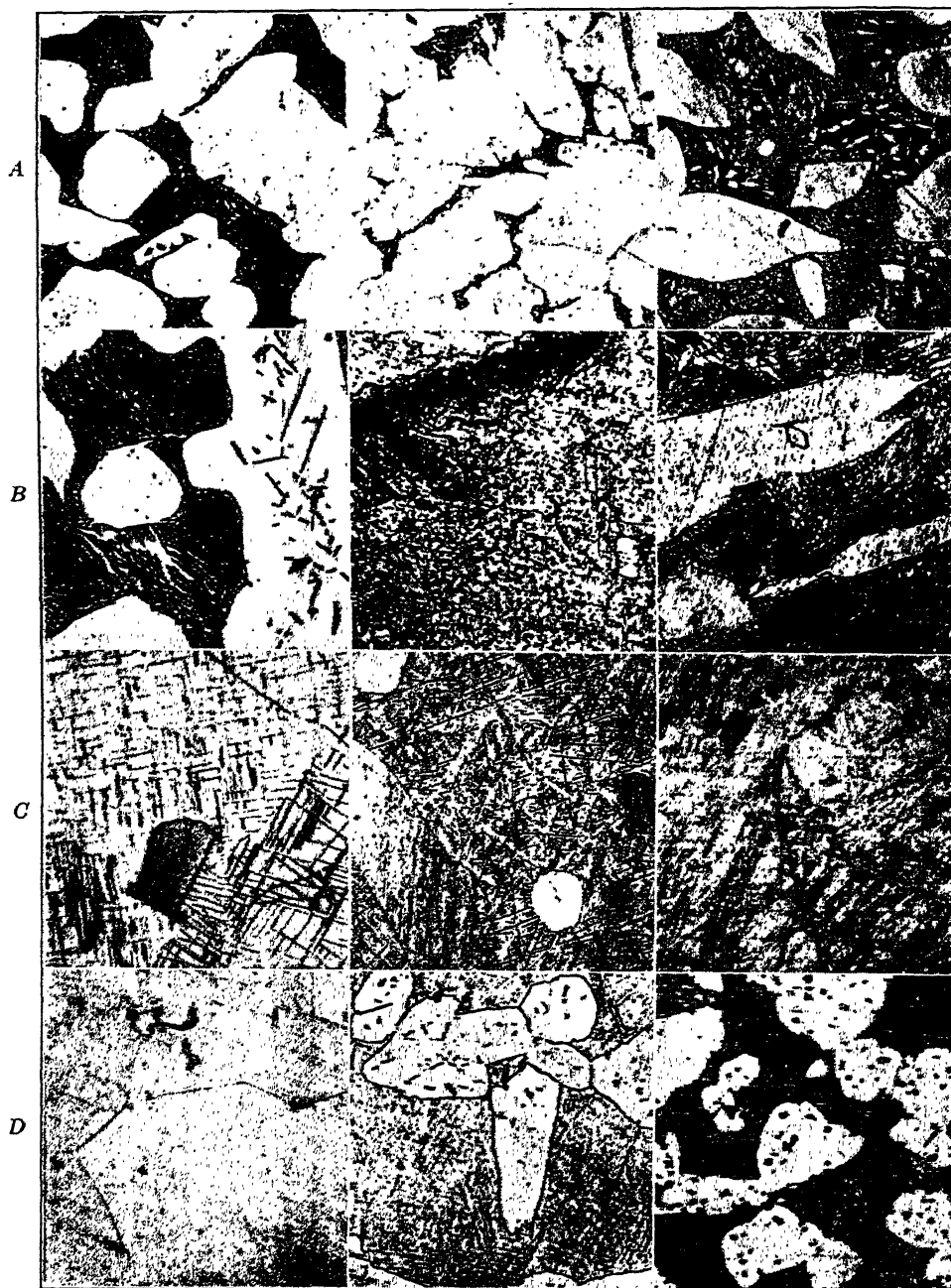
FIGS. 38–49.   CAPTIONS ON OPPOSITE PAGE.
A = Figs. 38–40.   B = Figs. 41–43.   C = Figs. 44–46.   D = Figs. 47–49.

position of beta into alpha at the cleavage planes of the beta, but a higher tempering temperature shows the beta completely transformed into alpha. Five per cent. silicon results in alpha plus partly decomposed eutectoid, but a higher temper shows a structure very similar to the annealed (Fig. 31). The alpha is striated in the same way, but the light yellow matrix now has a dark constituent present in it.

Figs. 59–70 show the structure of the alloys with 10 per cent. aluminum tempered at 400° C. and 650° C. Fig. 59 shows the normal structure of the aluminum bronze with 10 per cent. aluminum as tempered at 400° C. One per cent. iron, when added to the alloy and tempered at 400° C., introduces a few twins and the rod-shaped iron constituent in the grains of alpha, and the beta is just on the verge of decomposition. When this same alloy is tempered at 650° C., the structure becomes typical alpha plus the heavier needles of beta, which denote partial decomposition. One per cent. cobalt results in a heavily mottled structure of alpha showing a few twins, plus a relatively small amount of partly decomposed eutectoid. One per cent. manganese results in a structure of coarse beta which has mostly decomposed into alpha plus a little delta, when tempered at 650° C. A structure of large grains of eutectoid with excess alpha appears when 1 per cent. silicon is added to the alloy and the specimen has been tempered at 650° C. Five per cent. silicon, after a temper at 400° C., yields a structure apparently all alpha heavily mottled with the blue silicon constituent, but the same alloy if tempered at 650° C.

FIGS. 38–49.—STRUCTURES OF ALLOYS WITH 10 PER CENT. ALUMINUM, ANNEALED AND QUENCHED.

FIG. 38.—AL, 10 PER CENT.; NO ALLOYING ELEMENT. ANNEALED. × 100.
Alpha plus eutectoid.

FIG. 39.—AL, 10; CO, 1 PER CENT. ANNEALED. × 100.
Twinned alpha plus eutectoid. Cobalt particles in alpha.

FIG. 40.—AL, 10; MN, 1 PER CENT. ANNEALED. × 100.
Alpha plus eutectoid. Eutectoid partly decomposed.

FIG. 41.—AL, 10; NI, 5 PER CENT. ANNEALED. × 500.
Alpha plus eutectoid. Rod-shaped constituent in alpha due to nickel.

FIG. 42.—AL, 10; CO, 5 PER CENT. ANNEALED. × 500.
Alpha grains, slightly twinned; heavily mottled with particles of cobalt constituent. Large formation of cobalt constituent also present.

FIG. 43.—AL, 10; MN, 5 PER CENT. ANNEALED. × 500.
Alpha plus eutectoid. Manganese particles in alpha.

FIG. 44.—AL, 10; SI, 5 PER CENT. ANNEALED. × 500.
Precipitation of needles in alpha complete (Fig. 13). Free silicon present.

FIG. 45.—AL, 10 PER CENT.; NO ALLOYING ELEMENT. × 100.
Typical alpha plus beta. Quenched.

FIG. 46.—AL, 10; MN, 5 PER CENT. QUENCHED. × 100.
Large grains of beta with alpha as tiny light constituent.

FIG. 47.—AL, 10; SI, 5 PER CENT. QUENCHED. × 100.
Apparently all alpha, with free silicon present.

FIG. 48.—AL, 10; FE, 1 PER CENT. QUENCHED. × 100.
Alpha plus beta. Rod constituent present in alpha, due to iron.

FIG. 49.—AL, 10; FE, 5 PER CENT. QUENCHED. × 100.
Twinned alpha plus beta. Nodular iron constituent.
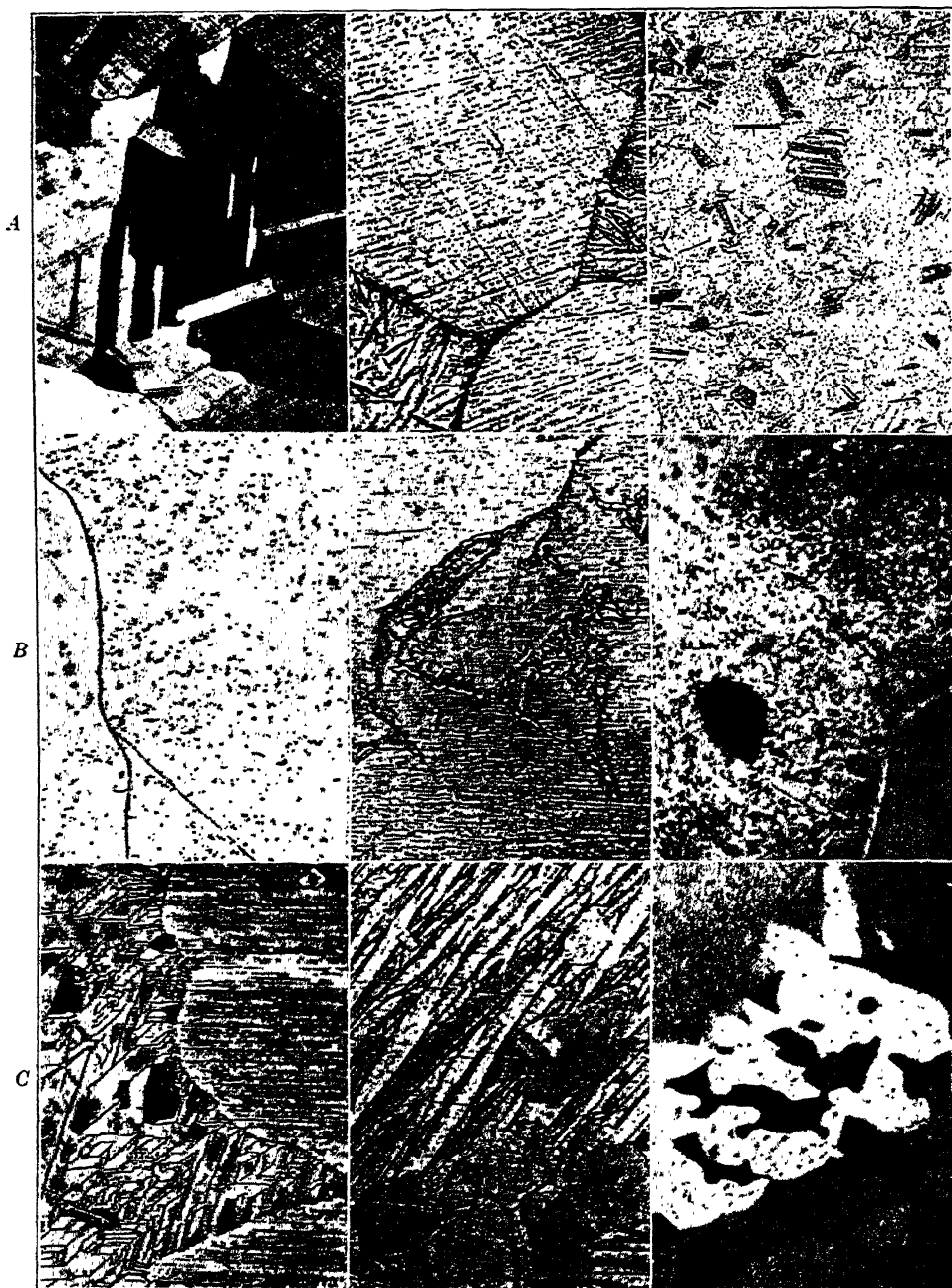
FIGS. 50–58.—CAPTIONS ON OPPOSITE PAGE.
A = Figs. 50–52. B = Figs. 53–55. C = Figs. 56–58.

shows small regular needles in the structure (Fig. 44).   The structure produced by adding 5 per cent. cobalt, when tempered at 650° C. also resembles the structure obtained when the alloy was annealed (Fig. 42) except that there are no twins in the alpha.   When the alloy with 5 per cent. manganese is tempered at 400° C., alpha may be seen precipitating from the cleavage planes of the beta which resulted from the quench.   Tempering at the higher temperature has completely resolved the beta into alpha plus eutectoid.

Figs. 71 to 82 show the structures of the alloys with 12 per cent. aluminum as quenched, as tempered at 400° C., and as tempered at 650° C.   Fig. 71 illustrates the typical acicular beta obtained when the normal alloy with 12 per cent. aluminum is quenched.   Five per cent. cobalt causes the formation of beta plus a considerable amount of alpha and, of course, the blue cobalt constituent when the alloy is quenched.   Quenching the alloy with 5 per cent. manganese produces a structure of brightly colored polyhedral grains with a few large needles across some of the grains.   This may be beta without the highly twinned condition which results in "needles."   Fig. 74 represents the decomposed condition of the beta in the normal alloy with 12 per cent. aluminum when tempered at 400° C.   The structure consists of alpha plus delta plus eutectoid plus a small amount of beta which has not been completely decomposed. The 1 per cent. manganese alloy when tempered at 650° C. shows small grains of eutectoid, partly laminated and partly granular, with excess alpha.   Tempering the alloy with 1 per cent. manganese at 650° C. results in the complete resolution of beta into its decomposition products— alpha plus delta plus eutectoid.   The alloy with 5 per cent. nickel is still mostly beta when tempered at 400° C., but after the higher temper-

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FIGS. 50–58.—STRUCTURES OF ALLOYS WITH 8 PER CENT. ALUMINUM.   DRAWN AT 400° C. AND AT 650° C.

FIG. 50.—AL, 8 PER CENT.; NO ALLOYING ELEMENT.   TEMPERED AT 400° C.   × 50.
Typical twinned alpha, plus very small amount of eutectoid.

FIG. 51.—AL, 8; SI, 1 PER CENT.   TEMPERED AT 400° C.   × 500.
Alpha, with faint twins, plus beta.   Mottled with blue silicon particles.

FIG. 52.—AL, 8; CO, 1 PER CENT.   TEMPERED AT 400° C.   × 100.
Tiny twinned grains of alpha, heavily mottled with blue cobalt constituent.

FIG. 53.—AL, 8; NI, 1 PER CENT.   TEMPERED AT 650° C.   × 50.
Alpha grains with mottlings due to nickel.

FIG. 54.—AL, 8; SI, 1 PER CENT.   TEMPERED AT 650° C.   × 500.
Alpha plus blue network constituent.   Beta completely decomposed.   See Fig. 51.

FIG. 55.—AL, 8; SI, 5 PER CENT.   TEMPERED AT 400° C.   × 500.
Alpha, large grains and small particles, plus delta.   Free silicon present.

FIG. 56.—AL, 8; MN, 5 PER CENT.   TEMPERED AT 400° C.   × 500.
Alpha plus partly decomposed beta, showing alpha precipitating from cleavage planes.

FIG. 57.—AL, 8; MN, 5 PER CENT.   TEMPERED AT 650° C.   × 500.
Beta almost completely decomposed into alpha.

FIG. 58.—AL, 8; SI, 5 PER CENT.   TEMPERED AT 650° C.   × 500.
Modified alpha showing striations.   Free silicon.   See Fig. 31.
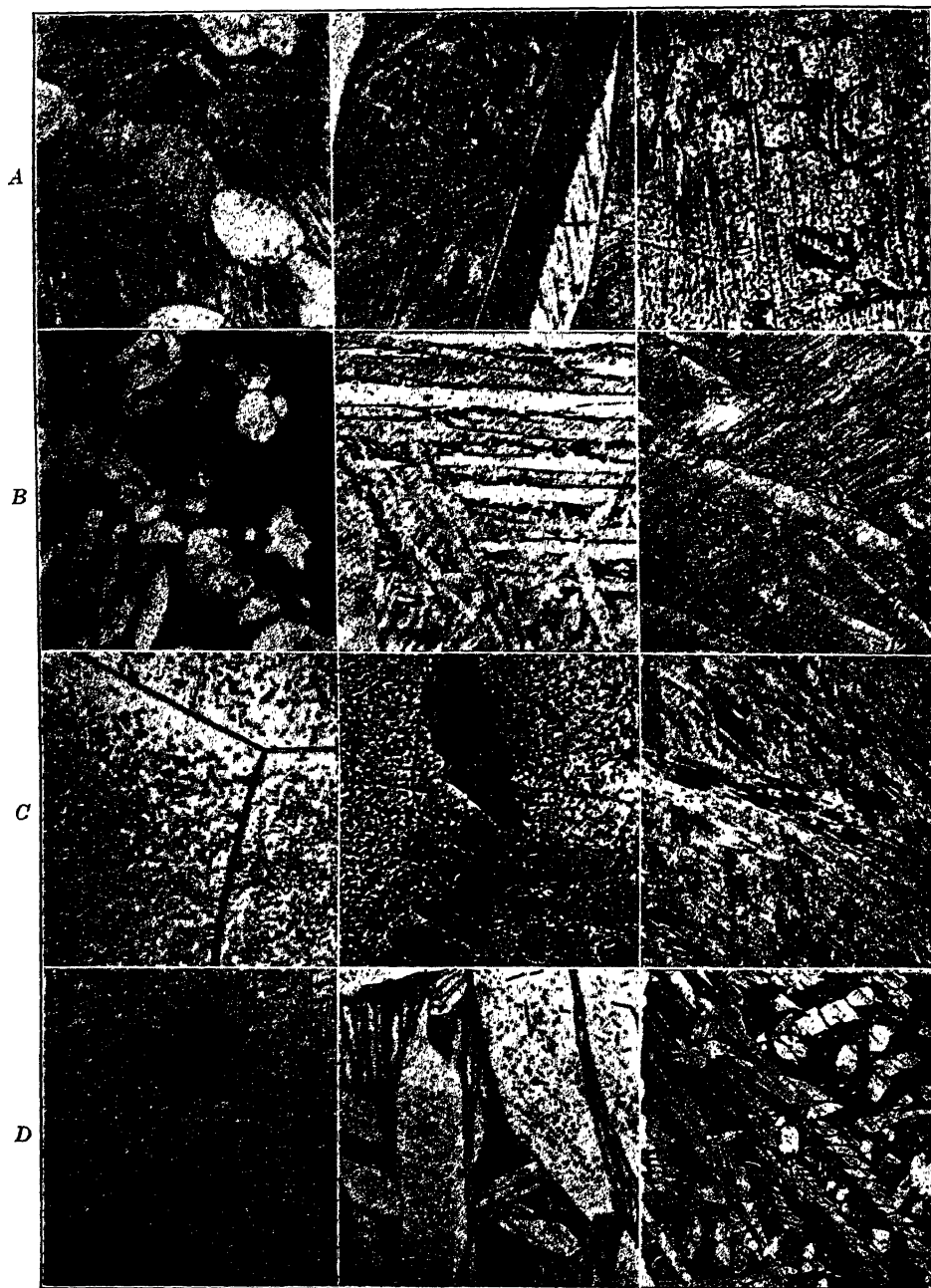
FIGS. 59–70.—CAPTIONS ON OPPOSITE PAGE.
A = Figs. 59–61. B = Figs. 62–64. C = Figs. 65–67. D = Figs. 68–70.

ing some areas of the specimen show alpha.   The 5 per cent. manganese alloy still shows beta after the high temper.   Five per cent. cobalt effects the complete breakdown of the beta from the quench (Fig. 72) into alpha plus delta.   The alloy with 5 per cent. nickel is still acicular beta after the temper at 400° C. but tempering at 650° C. decomposes the beta into alpha plus delta plus eutectoid.   Both these structures show the iron constituent.

From a systematic examination of the grain-size figures, the hardness tables and the microstructures of the various alloy systems, it has been possible to draw at least several generalizations as to the apparent effects of the various alloying elements on aluminum bronze.   These may be briefly summarized.

NICKEL-ALUMINUM-COPPER SERIES

Nickel inhibits the characteristic twinning of the alpha solid solution. It introduces a new rod-shaped constituent in the alpha grains, in the alloys with 8 and 10 per cent. aluminum and 5 per cent. nickel.   These rod-shaped forms are but little affected by heat treatment, and are probably a nickel-aluminum compound, since they are found only in the alpha grains.   Nickel did not effect any general decrease in grain size,

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FIGS. 59–70.—STRUCTURES OF ALLOYS WITH 10 PER CENT. ALUMINUM TEMPERED AT 400° C. AND 650° C.

FIG. 59.—AL, 10 PER CENT.; NO ALLOYING ELEMENT.   TEMPERED AT 400° C.   × 100.
Typical alpha plus beta.

FIG. 60.—AL, 10; FE, 1 PER CENT.   TEMPERED AT 400° C.   × 500.
Alpha plus beta.   Alpha shows a few twins, and contains blue particles due to iron.

FIG. 61.—AL, 10; CO, 1 PER CENT.   TEMPERED AT 650° C.   × 500.
Alpha slightly twinned, plus eutectoid.   Structure is heavily mottled.

FIG. 62.—AL, 10; SI, 1 PER CENT.   TEMPERED AT 650° C.   × 100.
Alpha plus duplex eutectoid.

FIG. 63.—AL, 10; FE, 1 PER CENT.   TEMPERED AT 650° C.   × 500.
Alpha plus partly decomposed beta.

FIG. 64.—AL, 10; MN, 1 PER CENT.   TEMPERED 650° C.   × 500.
Beta decomposed into alpha plus a little delta.

FIG. 65.—AL, 10; SI, 5 PER CENT.   TEMPERED AT 650° C.   × 500.
Evidently all alpha heavily mottled with free silicon.   Silicon also at boundaries.

FIG. 66.—AL, 10; CO, 5 PER CENT.   TEMPERED AT 650° C.
Apparently alpha mottled with blue cobalt constituent.   Also large forms of cobalt constituent present.

FIG. 67.—AL, 10; MN, 5 PER CENT.   TEMPERED AT 400° C.   × 100.
Alpha precipitating from cleavage planes of beta.

FIG. 68.—AL, 10; SI, 5 PER CENT.   TEMPERED AT 650° C.   × 500.
Mottlings in alpha have changed to needlelike structure.   See Fig. 65.

FIG. 69.—AL, 10; NI, 5 PER CENT.   TEMPERED AT 650° C.   × 500.
Alpha plus eutectoid.   Many particles in alpha due to nickel present.

FIG. 70.—AL, 10; MN, 5 PER CENT.   TEMPERED AT 650° C.   × 500.
Beta completely decomposed into alpha plus eutectoid.
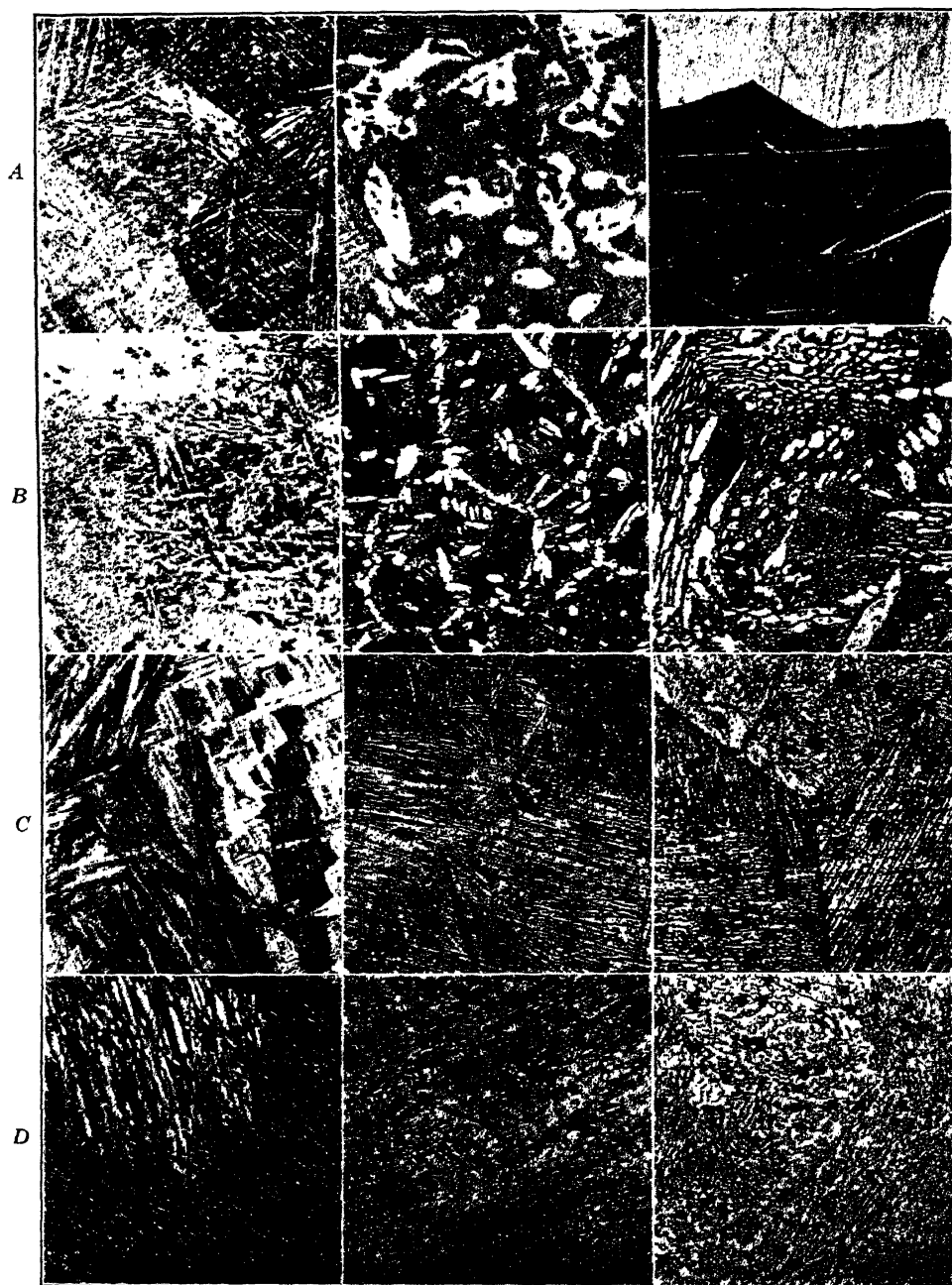
A = Figs. 71–73.   B = Figs. 74–76.   C = Figs. 77–79,   D = Figs, 80–82,

with the exception of the alloy with 12 per cent. aluminum and 5 per cent. nickel. Hardness results were erratic—in some cases the nickel proved an effective hardener; in others, negative results were obtained. It was not possible to correlate composition with either grain size or hardness.

MANGANESE-ALUMINUM-COPPER SERIES

Manganese promotes the formation of twins in the alpha solid solution. It causes the equilibrium diagram to shift to the left; or, in other words, each additional per cent. of manganese acts as an increase in the amount of aluminum. When added in amounts of 5 per cent., the manganese introduces a special constituent, readily recognizable as tiny primary crystals, light blue in color. Manganese acts as a powerful hardening agent and is also successful in reducing the heterogeneity of hardness of the alpha solid solution. It reduces the grain size, in general; very drastically in some of the specimens.

IRON-ALUMINUM-COPPER ALLOYS

Iron increases the tendency of the alpha solid solution to form twins, but only after quenching. When present in amounts of 5 per cent., the iron forms a new constituent, cruciform or nodular in shape, which is relatively unaffected by heat treatment. Iron reduces the grain size

FIGS. 71–82.—STRUCTURES OF ALLOYS WITH 12 PER CENT. ALUMINUM, AS QUENCHED, TEMPERED AT 400° C. AND AT 650° C.

FIG. 71.—AL, 12 PER CENT.; NO ALLOYING ELEMENT. QUENCHED. × 50.
Typical beta.

FIG. 72.—AL, 12; CO, 5 PER CENT. QUENCHED. × 100.
Alpha plus beta plus blue cobalt constituent.

FIG. 73.—AL, 12; MN, 5 PER CENT. QUENCHED. × 50.
Brightly colored polyhedral grains with needles running across grains (perhaps beta?)

FIG. 74.—AL, 12 PER CENT.; NO ALLOYING ELEMENT. TEMPERED AT 400° C. × 100.
Eutectoid plus alpha plus delta plus beta.

FIG. 75.—AL, 12; CO, 1 PER CENT. TEMPERED AT 650° C. × 100.
Small grains of eutectoid with alpha at grain boundaries.

FIG. 76.—AL, 12; MN, 1 PER CENT. TEMPERED AT 650° C. × 500.
Shows decomposition products of beta: alpha plus delta plus eutectoid. Manganese constituent present.

FIG. 77.—AL, 12; NI, 5 PER CENT. TEMPERED AT 400° C. × 100.
Beta only slightly decomposed. Alpha beginning to precipitate from cubic cleavage planes.

FIG. 78.—AL, 12; MN, 5 PER CENT. TEMPERED AT 650° C. × 100.
Large grains of beta, with clusters of manganese constituent.

FIG. 79.—AL, 12; FE, 5 PER CENT. TEMPERED AT 400° C. × 500.
Large grains of beta, with nodular iron constituent.

FIG. 80.—AL, 12; NI, 5 PER CENT. TEMPERED AT 650° C. × 100.
Large grains of beta, partly decomposed, showing some alpha.

FIG. 81.—AL, 12; CO, 5 PER CENT. TEMPERED AT 650° C. × 100.
Much cobalt constituent. Alpha plus some eutectoid.

FIG. 82.—AL, 12; FE, 5 PER CENT. TEMPERED AT 650° C. × 500.
Beta completely decomposed into alpha plus delta plus eutectoid. Nodular iron constituents present.

materially in all of the alloys.   The hardness results of this series were somewhat erratic—some of the alloys responded to heat treatment in opposite ways—but the general effect was an increase in hardness. Iron has made little change in the microconstituents, indicating that it does not add to the aluminum content as does manganese.   In other words, its "coefficient of equivalence" with respect to aluminum in aluminum bronze is practically zero.

Cobalt-aluminum-copper Alloys

The most remarkable characteristic of this series of alloys is that cobalt has a slightly negative "coefficient of equivalence;" that is, additions of cobalt cause a decrease in the aluminum content.   The chemical compositions of these alloys listed in Table 1 show that the cobalt and the aluminum contents are rather irregular, but a careful study of the microstructures indicates that the generalization made above is sound.   Cobalt has had little effect on the grain size, except in a few isolated cases.   The hardness of the alloys has been appreciably increased, on the whole.   The cobalt introduces a new constituent, slate blue and very hard, which, in the alloys with 1 per cent. cobalt, occurs in the form of small round or rod-shaped particles and in the alloys with 5 per cent. cobalt as a cuneiform or vertebraelike structure.

Silicon-aluminum-copper Alloys

One per cent. silicon increases the twinning characteristic of the alpha solid solution.   It gives the eutectoid a new bluish color.   Silicon seems to have an appreciable "coefficient of equivalence," especially in the alloys with 8 and 10 per cent. aluminum.   Five per cent. silicon, however, produces a great change in the appearance of the alpha solid solution, causing striation of different shades of color and different directions in the same grain, and also transforms the eutectoid into a yellow constituent.   Quenching shows a characteristic alpha present. In the 10 and 12 per cent. alloys a small needlelike constituent is found, which resembles beta somewhat.   Grains were excessively large, except in the alloy with 8 per cent. aluminum and 1 per cent. silicon.   All the alloys with 5 per cent. silicon were so brittle and lacking in cohesion between the grains that they went to pieces and could not be tested for hardness.   The alloys with 1 per cent. silicon show a high hardness.

DISCUSSION

(W. R. Webster presiding)

G. F. Comstock, Niagara Falls, N. Y.—It might be worth while to bring out the fact, a little more than the authors have done, that their quenching temperature for the 10 per cent. aluminum alloys was from the alpha plus beta field rather than from the pure beta field.   In the commercial heat treatment of such alloys it is well to

raise the quenching temperature so that all the primary alpha is dissolved in the beta before quenching.

The structures shown in Figs. 45 and 50 bring out the fact that some primary alpha remains in the alloy, so that these structures are really not typical of the structures that should be obtained in the best commercial practice of quenching and heat treatment of 10 per cent. aluminum bronze. The presence of the primary alpha will decrease the hardness in a quenched alloy, and in the quenched and tempered material would more or less impair the physical properties.

H. A. ANDERSON, Chicago, Ill.—It seems to me that repeated contributions of this type to the Institute are slowly building up a metallographic encyclopedia of American origin. A great deal of work of this kind has been done abroad, and more and more of it is being done here. Papers of this sort assist works' metallurgists to identify new structures which they may encounter in connection with studies designed to improve the quality of castings or to diagnose the cause for failures.

F. T. SISCO (written discussion).—This investigation was undertaken by the U. S. Army Air Corps in an attempt to increase the hardness of aluminum bronze used for valve seats and valve guides for aircraft engines. So far as I know, the Army has not adopted any of these alloys as a standard. The research work covered by this paper was in the nature of an exploration of the field to determine, if possible, whether any of the alloys within the range of compositions investigated showed sufficient promise to warrant further study. A tremendous amount of further work would be necessary before any of the alloys could be used as a standard.

Metal Working in Power Presses

By E. V. Crane,* New York, N. Y.

A tremendous volume of the metal rolled annually into sheets strips and coil stock finds its way to a host of stamping and manufacturing plants which are the quantity production units of the country. Considerable in volume, too, are the rolled and extruded rods which go into forging and manufacturing plants for conversion into the same general line: those widely sold metallic necessities and luxuries of the household, the office, transportation, farming and building construction.

Yet, in spite of its age and its importance, the stamping trade has been doing its "engineering" largely by trial and error. Its distinctive method is *shearing out* and *plastically working* metal to finished shape in a few quick strokes with high loads and expensive tools which are warranted only by large quantities to be produced.

The principal operations have many features in common with rolling and wire-drawing methods. Combinations of stresses are different, however, and details of operations are infinite in variety. An engineering study of the subject begins with stress analysis, but must go back to metallurgy for its foundation.

A grouping of pressed-metal working operations according to whether the metal is (1) sheared, (2) bent, (3) drawn or (4) squeezed has proved useful. All of these groups include instances of both hot and cold operations. For discussions of metal working properties, the division between hot and cold working is taken as the recrystallization range of temperature. This, of course, brings tin, lead and often zinc into the hot-work range at or near room temperature. The outstanding hot-working press field is in forging: particularly of brass; all of which is included in the squeezing group.

Shearing Operations

The shearing group of operations, including blanking, piercing, trimming, shaving, slitting, shearing, notching, parting and numerous variations and combinations of these enters once or more into the production schedule of practically every stamped or forged article. The transverse stress, set up in shearing, as shown in Fig. 1A, is a combination of an angular compressive thrust and a tensile stress which is also at an

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* Staff Engineer, E. W. Bliss Co.

angle.   The surface material is the most severely stressed because it is being drawn or stretched over the cutting edges.   Accordingly, when a local ultimate is reached along these edges, fractures start from the opposing sides and spread quickly, as illustrated in Fig. 1B.

Fig. 2 shows three photomicrographs illustrating the effect of shearing stresses upon the crystal structure of the metal in shear.   The sample selected was ¼-in. Tobin bronze strip as received (Table 1), which has been partially strain-hardened.   The shearing punch penetrated approximately 17.5 per cent. of the metal thickness, at which time the maximum stresses had just been passed and the fracture had started at the points where the cut was approximately tangent to the grain or direction of rolling.   The fracture had hardly started, however, where the cut was across the grain.
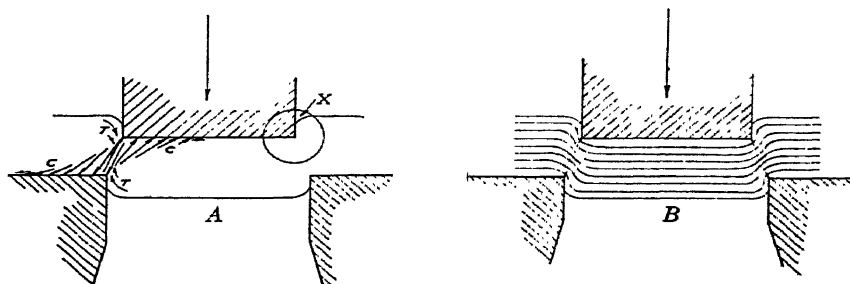
FIG. 1.—SECTIONS OF A BLANK DURING SHEARING.
A. STRESS DIRECTIONS.   B. METAL MOVEMENT.

The photomicrographs were taken at the encircled point x in Fig. 1A. Fig. 2A shows the surface profile of the metal and the position of the corner of the piercing punch.   As this photograph was taken on a section with the grain of the metal, it shows well the severe distortion that takes place before the fracture starts.   Fig. 2B also shows a section cut with the grain or the direction of rolling and gives an idea of the grain distortion along the working surfaces and in the severely worked area where the fracture will form.   As a matter of fact, a slight fracture has already occurred, forming a burr due to dullness of the cutting edge.   Fig. 2C was taken of a section across the grain of the metal where the line of fracture was tangent to the direction of rolling.   This is evident in the fact that the grains are equiaxed instead of being elongated.   Note also that the upper edge of the sheet did not drag down with the punch and that the fracture really began when the punch had progressed perhaps halfway to the position shown.   This is found by examination of the vertical side wall.   The fracture in this case had extended almost one-quarter of the way through the blank.

The term "shearing" applied to pressed-metal cutting operations should not be confused with the torsional stress described as "shear"
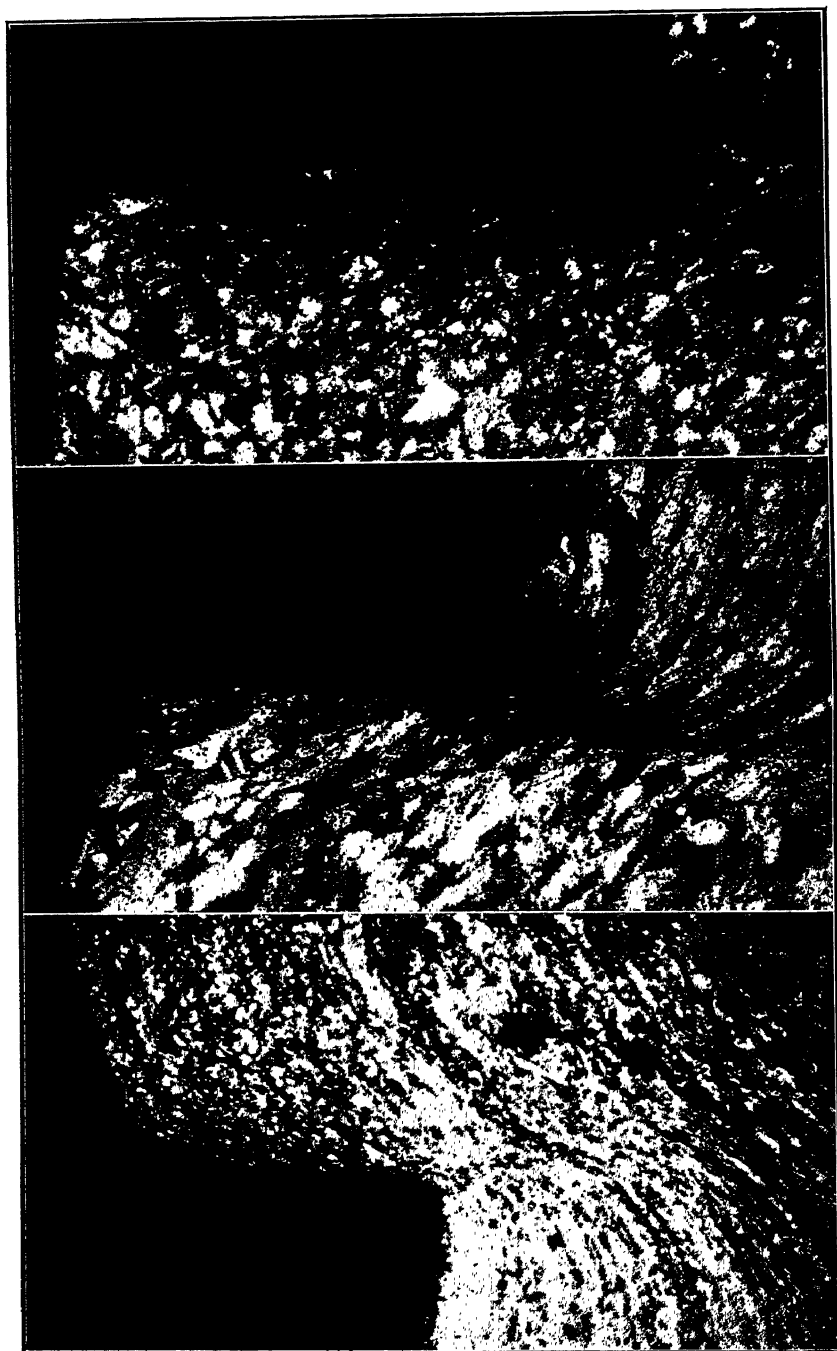
FIG. 2.—TOBIN BRONZE 17 PER CENT. SHEARED AS AT X IN FIG. 1, SHOWING PROFILE AND STRESSED AREA.

A, with the grain, indicates metal movement. × 90.
B with the grain and C across the grain (× 100) show directional effect upon the crystals and the resistance of the metal.

which, in physical tests, is usually given as greater than the tensile ultimate. The "resistance to shearing" or blanking, on the contrary, is lower than the tensile figures both as to yield point and ultimate. The nominal ultimate resistance to shearing (based on original area in shear) for Tobin bronze, for example (Table 2), is a little under two-thirds of the nominal "ultimate tensile."

Table 1, showing the resistance to shearing in the annealed and strain-hardened states, and the penetration required to start the fracture, is compiled tentatively from our experiments and such meager published data as we have found. The strain-hardened state (as received) is, of

TABLE 1.—*Approximate Resistance to Shearing in Dies*

Material	Annealed State		Partially Cold-worked[a]	
	Resistance to Shearing, Ss. Lb. per Sq. In.	Reduction in Area, Per Cent.	Resistance to Shearing, Ss. Lb. per Sq. In.	Reduction in Area, Per Cent.
Lead..............	3,500	50	Anneals at room temperature	
Tin...............	5,000	40	Anneals at room temperature	
Aluminum.........	8,000	60	13,000	30
Zinc..............	14,000	50	19,000	25
Copper............	22,000	55	28,000	30
Brass..............	32,000	50	52,000	20
Bronze 90–10			40,000	
Tobin bronze.......	36,000	25	42,000	17
Steel 0.10 C.......	35,000	50	43,000	38
0.20 C.......	44,000	40	55,000	28
0.30 C.......	52,000	33	67,000	22
0.40 C.......	62,000	27	78,000	17
0.60 C.......	80,000	20	102,000	9
0.80 C.......	97,000	15	127,000	5
1.00 C.......	115,000	10	150,000	2
Silicon steel........	65,000	30		
Nickel.............	35,000	55		

[a] As received. Actual "degree of cold working" due to previous treatment unknown.

Available test data do not agree closely. This table is subject to verification with closer control of metal analysis, rolling and annealing conditions, die clearances, etc.

course, open to considerable variation, and should probably be graded. Better data along this line would certainly be of value to the industry.

Fig. 3 shows the results of a typical shearing test of No. 11 gage, 0.125-in. yellow brass. An Olsen recording testing machine is used, equipped with a small die set. The die was of 1.591-in. dia., and the punch selected was such as to give a clearance of 10 per cent. of the metal thickness between the punch and die all around.

The three curves of Fig. 3 are reproduced as recorded but the scales are arranged to read in unit stress based on the original area in shear plotted against percentage reduction of this area as the punch penetrates the material. Curve A is from No. 8 hard or spring temper brass as rolled, measuring 91 Rockwell B scale ($\frac{1}{16}$-in. ball and 100 kg. wt.)
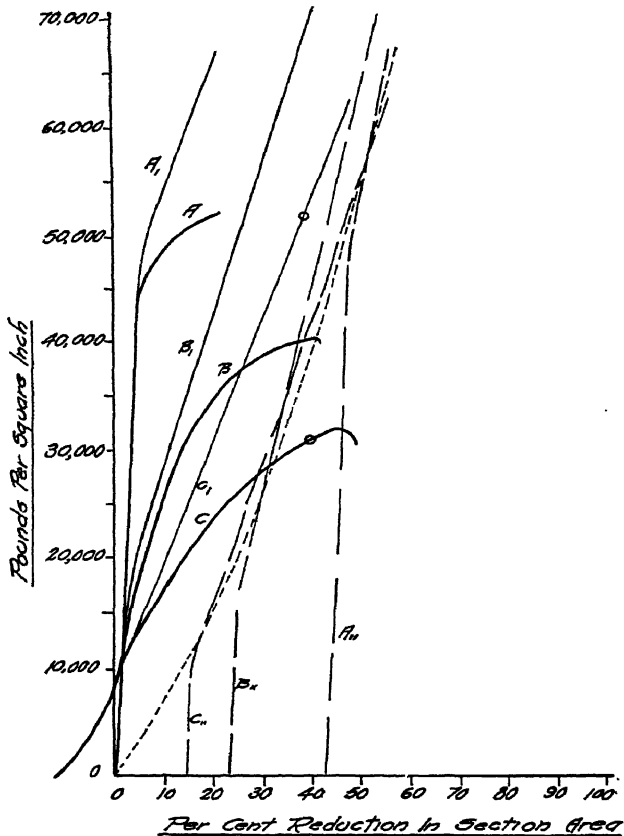
FIG. 3.—SHEARING OR BLANKING TEST CURVES OF 70:30 BRASS.

A, No. 8 hard; B, partially annealed; C, annealed; then relocated at A_1, B_1 and C_1 to read in unit stress as the area is reduced; and finally transposed to establish a common curve for any state.

.or 190 Brinell, and failed at about 54,000 lb. per sq. in. and 22 per cent. penetration. Curve B is from the same material partially annealed. Curve C is again the same material annealed at 1100° F. for $\frac{1}{2}$ hr. to a Brinell hardness of 58. It failed at approximately 34,000 lb. per sq. in. and a punch penetration of 49 per cent.

The three recorded curves have been replotted at A_1, B_1 and C_1 to show the actual rise in resistance of the metal as the area in shear is

reduced and the material in the pressure area is distorted and strain-hardened. These are derived by taking points, say, every 5 per cent. of reduction along the recorded curves and dividing the recorded unit stress by the decimal portion of the metal thickness remaining in shear and plotting the new (actual) unit stress at that depth. Thus, on curve C, at 40 per cent. penetration (or 0.60 times the metal thickness remaining in shear), the recorded stress was equal to approximately 30,800 lb. per sq. in., and this divided by 0.60 gives the actual unit stress of about 51,300 lb. per sq. in. as one of the points on the new curve C_1. There is necessarily some error in transferring and transposing which amounts in extreme cases to perhaps 5 per cent.
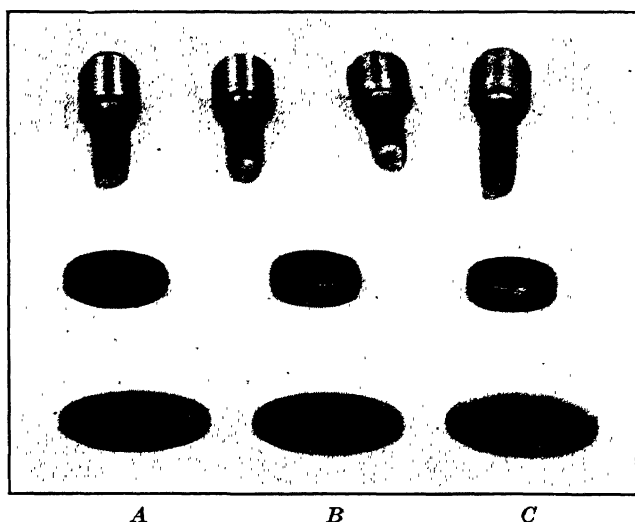
FIG. 4.—TYPICAL TENSILE, COMPRESSION AND BLANKING TEST SPECIMENS.
The latter illustrate increasing deformation and increasing penetration to effect shearing as metal becomes softer.

The three actual unit stress curves have a more or less common trend, and failure occurred, as it happened, at about the same unit stress. The three curves, A, B and C, were then transposed to the right in an attempt to unite them in a common curve, suggested by short dashes, in an effort to indicate a "rate of strain-hardening" curve. More satisfying results were obtained, however, with a combination of tensile and compressive tests, as will be shown later. Somewhat similar results have also been obtained in shear tests of aluminum and steels.

Fig. 4 shows the three blanks or disks cut in producing respectively the three curves A_1, B_1 and C_1. Note the increase in width of the burnished band, and decrease in width of the fractured area (Fig. 1B) as the material becomes softer and the percentage of penetration to effect shearing

increases. The effects of the tensile and compressive stresses illustrated in Fig. 1 are also easily found in the soft blank, *C*, in the form of (1) a flattened area near the edge on the compression side, (2) a rounded and slightly roughened area around the edge on the tension (burnished) side, and (3) a general bowing of the whole blank. This bow is reduced in the harder blanks and is also reduced with less die clearance. Micro-examination shows that the roughening in the tension area is due to the tipping of surface crystals as the metal is distorted.

For operations strictly within the blanking group, previous treatment of the metal with reference to strain-hardening does not make as much difference as it does in all of the other groups. However, the harder the metal, the flatter will be the blank and the less the rounding at the tension edge. Greater hardness also admits of less clearance which, again, makes for a flatter blank. The more the material has been strain-hardened in its previous working, the higher will be the shearing resistance, as shown in Fig. 3. Some slight increase in shearing resistance in ound with a decrease in clearance between cutting edges.

The material at the edge of blank is necessarily hardened in the shearing action and especially along the border of the burnished area adjacent to the fractured surface, Fig. 4. This fractured surface is a potent source of further fractures if the metal along the edge is subject to severe or repeated tensile stress in subsequent operations or applications. It is also thought to furnish the starting point for season cracking in material reduced severely in drawing. It is possible, by using punches and dies with little or no clearance, to obtain an edge surface which is entirely burnished and apparently free from fractures. Secondary shearing fractures are almost certain to have formed, however, even though more or less concealed by the burnishing.

BENDING

Plain bending operations are simple in nature, but offer a number of points interesting to a discussion of metal working. In making a bend, the metal is naturally stressed in compression on the inner surface and in tension on the outer surface. As the cross-section area in compression tends to increase and that in tension tends to decrease, the principal movement is in tension, and the metal thickness is materially reduced at the bend. The sharper or smaller the inside radius is made, the greater is the reduction in thickness at the bend. Fig. 5 has been drawn to illustrate the distortion of the metal which takes place in making a bend.

Previous treatment of the metal is usually of importance in that the bracket, frame, hinge, lever, or what-not usually requires stiffness and is made of metal that has been strain-hardened in rolling to a fairly hard state. With such material, the sharper the bend, or the harder the metal,

the greater is the likelihood of fracture in bending or subsequently in fatigue due to vibration.

The preparatory strain-hardening of the metal has given it directional properties so that it is softer and more ductile for bends made on an axis or line across the direction of rolling than for those made on an axis paralleling the direction of rolling. Tensile tests of rolled zinc by Meyer,[1] for example, showed a yield point of 11,400 lb. per sq. in. with the grain and 13,600 lb. per sq. in. across the grain.

For this reason blanks are usually laid out, on strip material, so that the bends will come across the "grain." This is often distinctly detrimental to scrap economy or unfavorable to layouts for automatic production.

In a recent example of a rifle clip spring, No. 8 hard spring brass was specified. The economical and desirable layout from the production standpoint required that a subsequent bend be made with the grain. It was shown, however, that, in this direction, the part would not stand consistently the required 90° bend and reversal, whereas, across the grain, it would stand the bend and three to five reversals.
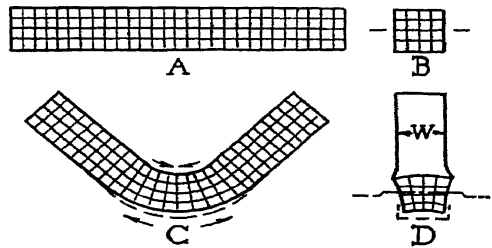
FIG. 5.—METAL MOVEMENT IN BENDING, ILLUSTRATING REDUCTION IN THICKNESS.

In this connection, the patented Steckel process[2] of rolling is being watched with interest, as it is claimed that, by pulling the stock through the rolls, the combination of tensile and compressive stresses produces a more uniform strain-hardening without directional differences. It may also be noted, however, that one of the mills equipped with the process. when asked to furnish metal free of directional preference for the job just discussed, said that it was not yet prepared to say it could be done.

Strain-hardened material shows a proportionally high elastic limit. This means that, in bending metal past a corner, an overbend must be made to compensate for the spring-back, which varies with the hardness of the metal. An alternative is to strike or coin the metal (especially in a V-die) sufficiently to set up compressive stresses which will balance the tensile stresses on the outer surface of the bend and "set" the angle.

DRAWING

The drawing group of press operations is perhaps the most interesting of the four groups from the standpoint of metal working. It combines

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[1] O. Meyer: *Oesterreich. Ztsch. f. Berg- und Huttenwesen* (1905) **53**, 522, 538. Table reprinted by H. F. Moore: An Investigation of the Strength of Rolled Zinc. Univ. Illinois Eng. Expt. Sta. *Bull.* 52 (1911) 7.

[2] A. P. Steckel: U. S. Patents 1744016, 1744017, 1744018, Jan. 14, 1930.

an initial tensile stress with an often much higher resultant compressive stress to produce severe rearrangements usually equivalent to the necking range in the tensile test. Redrawing operations often carry the metal to a point where commercially expensive, and often unsatisfactory, annealing operations are required to recrystallize it to a state that will permit further working.

The group includes the drawing of round, rectangular and irregular shapes, reducing or redrawing of deep shells, stretching of shallow shapes, and ironing to reduce wall thickness. Burring and necking operations are closely allied to it, and curling and bulging a little more distantly. As this paper is being limited to a theoretical discussion of only the typical metalworking operations, it will be necessary to omit specific consideration of the last four operations mentioned, and, also, the drawing of rectangular and irregular shapes. The odd shapes create new problems in almost every instance, but the principles[3] remain generally similar to those involved in drawing simple round shells.

Fig. 6 shows a series of shells drawn, or partially drawn, from blanks marked off in squares so that the metal movement would show in distortion of the squares. Those in the bottom of the shells are not changed in shape. Toward the edge they become narrower in proportion to the reduction in diameter and longer radially. One blank was marked with radial lines from its center, which, when it was drawn up, became parallel lines on the shell wall.

Fig. 7 is arranged to illustrate drawing, redrawing or reducing, ironing or wall reducing of simple round shells. In each case the shell is shown as partly drawn through to illustrate the metal movement.

The original diameter of the flat disk, or blank, before drawing, Fig. 7A, has been indicated in the partial plan view. On this an arbitrary area, a section of a ring 15° wide, has

FIG. 6.—MOVEMENT OF METAL IN DRAWING ILLUSTRATED BY BLANKS MARKED WITH SQUARES, EXCEPT THE INVERTED SHELL, WHICH WAS MARKED WITH RADIAL LINES.

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[3] An extended general discussion by the author, entitled Press Working and Forming of Metals, was begun in *Metal Stampings*, June, 1928.

been indicated in dotted lines. As the draw progresses, this area becomes narrower circumferentially in proportion to the reduction in diameter of the shell, and as indicated by its new position, shown in solid lines.

In the course of the movement, it has become wider radially, and thicker in an inverse ratio to the square root of the change in diameter. In thus being worked, the initially unstrained crystals have been broken up into smaller crystal fragments. As these are not as closely packed as the unstrained material, the volume is slightly increased. This change is so small, however (0.1 to 1 per cent. in extreme cases), that volume can be used as the constant in computing changes and plotting movement.

Returning to Fig. 7A, note the arrows placed to indicate the compressive stresses in the flange, which are the immediate cause of the
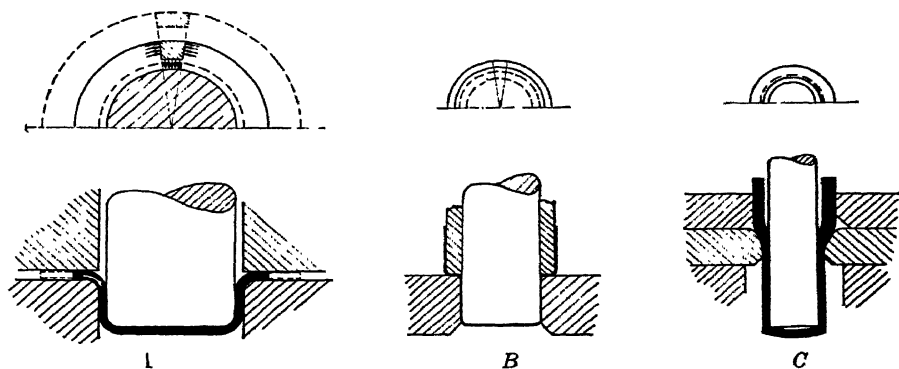
FIG. 7.—METAL WORKING.

A, in drawing; B, in redrawing or reducing; C, in ironing or wall reduction.

reduction in width of the elemental area and therefore the reduction in circumference of the blank. These forces begin the plastic working of the metal when they reach a magnitude equal to the yield point of the particular piece of metal, and rise as the resistance of the metal rises with strain-hardening.

These primary compressive stresses in the flange are the direct result of normal tensile stresses over the drawing edge which are related to them in the ratio of $(D-d)/D$. In this, D is for blank diameter and d for shell diameter. Accordingly, a 50 per cent. reduction, when d equals $D/2$, will require a tensile stress equal to the compressive stress and therefore equal to the yield point to start movement. As the reduction is made less (than 50 per cent.), the tensile stress necessary to create a sufficient compressive stress becomes less and less, so that, for a shallow shell, the drawing load on the punch is relatively low. It may be noted that the drawing load is made up, not only of the stress necessary to reduce the flange, but of an allowance to take care of bending the metal

over the drawing edge, and another allowance for friction on the blank-holding surface.

Accordingly, at 50 per cent. reduction in drawing, the tensile or drawing load in the shell wall is materially above the yield point and approaching the necking range. When this is reached, the bottom of the shell will tear out. Therefore, 45 to 50 per cent. reduction in diameter is the usual commercial limit for the first draw, although blankholding conditions may reduce it farther, especially where the metal is very thin compared with the diameter.

Fig. 7B illustrates a double-action reduction of a shell previously drawn in a die such as is shown at A. The term "double action" refers to the use of a blankholding ring to hold flange flat and prevent the formation of wrinkles, its action being controlled with reference to the drawing punch. A similar ring was shown in Fig. 7A. Wrinkles apparently start because of nonuniform resistance to the reducing compressive stresses in the upper and lower surfaces of the metal in the flange area. When the metal is thick relative to the diameters, no blankholding is required. As it becomes relatively thinner, an increasing pressure must be applied but, at most, this does not approach the yield point. An exception to this is found in some shallow forms where the edge must be pinched tightly to stretch rather than draw the shape.

Comparison of the plan views indicates that reducing is similar in action to drawing, except that the wall of the original shell serves as a reservoir to feed metal into the flange area where the reduction is accomplished. The bend from this old wall into the flange places an added tensile load upon the new shell wall and places a top limit of about 35 per cent. per operation upon commercial reductions.

Single-action reductions (without blankholder) may go a little higher if stepped dies may be used to prevent wrinkles. The normal construction, without the step, is usually limited to 20 or 25 per cent. reduction per operation.

In ironing, Fig. 7C, there is a combination of a slight reduction (single action) with considerable wall thinning. Accordingly, the unit volume in the wall is stressed in compression in two directions, width and thickness, as in wire drawing. It therefore suffers greater elongation than in plain drawing where it is permitted to thicken up. As in drawing, the balance of tensile and resultant compressive stresses makes a total reduction of 50 per cent. (elongation of 100 per cent.) the approximate limit per operation.

CARTRIDGE CASE REDUCTIONS

As a specific example of metal working in drawing, photomicrographs have been prepared of a small arms cartridge shell which is made of 70:30 soft drawing brass. Fig. 8 shows the series of operations in

producing it. First, it is blanked from the strip and drawn into a cup
with a slight wall reduction, and annealed and pickled.   Then it under-
goes four reductions which are largely ironing, and is annealed after each,
bringing it to the stage at which the photographs in Fig. 10 were taken.
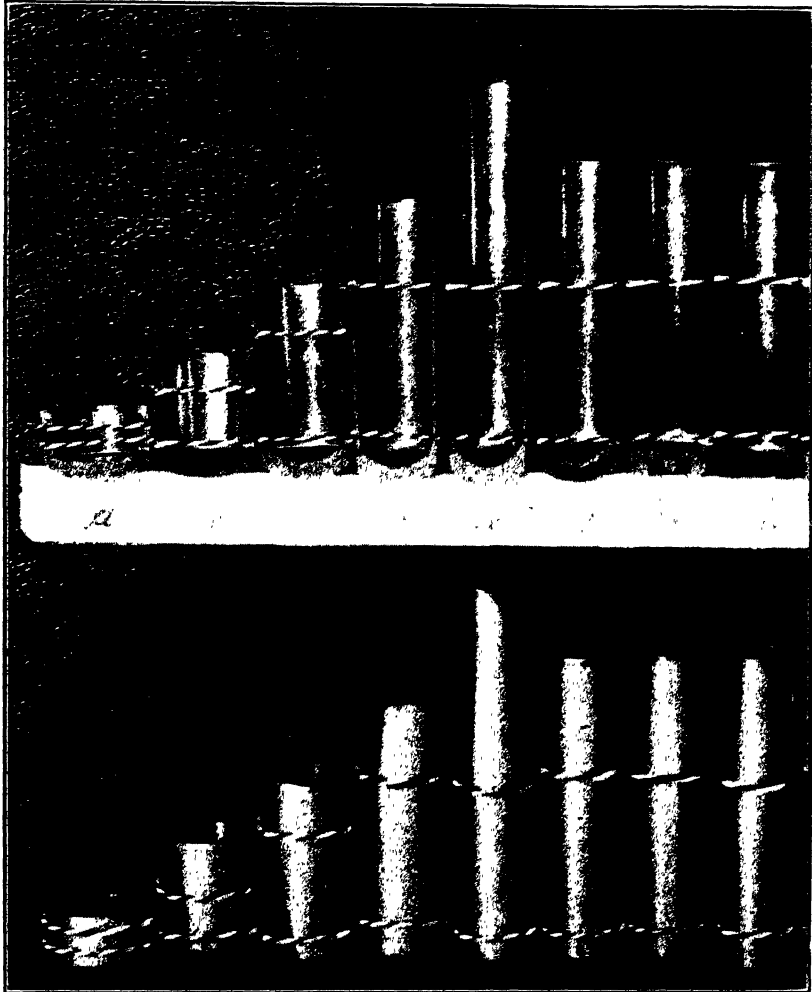
FIG. 8.—OPERATIONS IN THE PRODUCTION OF SMALL ARMS CARTRIDGE CASES, 70:30
BRASS.

Fig. 9 illustrates the change of shape wrought in reducing from blank
to shell.   A unit volume of metal at the edge of the blank has been worked
out, as shown by the shaded areas, until it has been elongated about
1300 per cent., or reduced by the equivalent of 93 per cent.
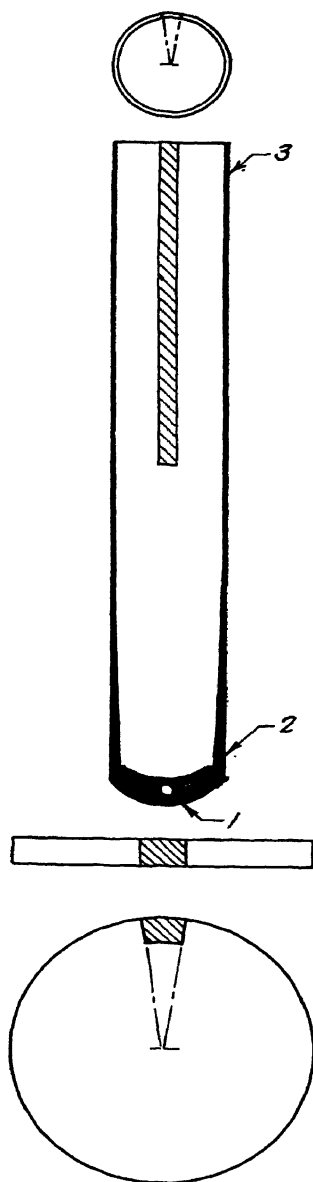
FIG. 9.—PROPORTIONS OF CARTRIDGE SHELL AND BLANK.

Metal movement is indicated by shaded areas. Figures 1, 2 and 3 show places at which photomicrographs were taken.

The physical specifications of the brass called for an elongation (general) of 52 per cent. in 2 in. The actual reduction per step amounted to nearly 50 per cent., which is the equivalent of nearly 100 per cent. elongation. This brings the stresses at each reduction clearly into the range found in the necked portion of a tensile specimen. The numbers 1, 2 and 3 in Fig. 9 indicate the approximate points on the section surface of a half shell at which photomicrographs were taken.

Fig. 10 shows a group of photomicrographs of cartridge cases, in the strain-hardened state after the fourth drawing operation and as annealed in preparation for the next operation. These were taken at 100 magnifications after etching for $\frac{1}{2}$ to $\frac{3}{4}$ min. in a solution of about one part hydrogen peroxide in twenty parts ammonium hydroxide. The annealing was the regular production operation in which the shells take 7 to 8 min. passing through an electric furnace heated to 1300° F. The foregoing data apply also to the extruded cartridge case photomicrographs, Fig. 21.

Figs. 10A and 10C were taken before and after annealing respectively, at or near point 1 at the bottom of the shell. Figs. 10B and D, taken near point 3 in the shell wall, also represent the state before and after annealing respectively.

In comparing the photographs, note that the previous annealing brought the grains to a fairly large size, favorable to a moderately severe operation. Both of the worked samples show clearly the old grain boundaries; the grains, however, showing many slip movement lines and considerable distortion along the normally straight boundaries of the twins. The wall section naturally shows evidence of the severest working.

Fig. 10E, taken through a green filter, shows more clearly than 10B the numerous (parallel) slip planes which mark the movement and break up the old crystals into many tiny fragments.
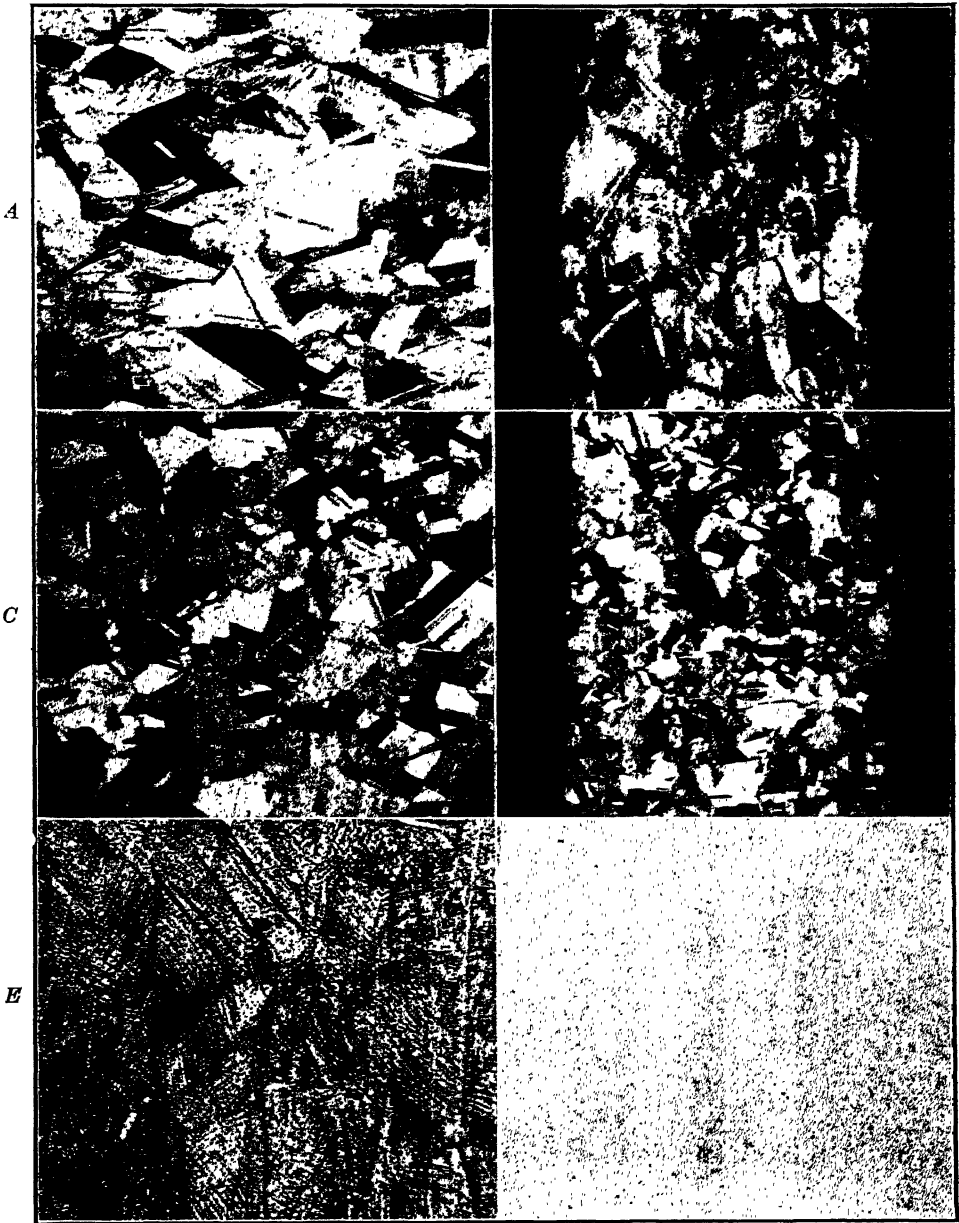
FIG. 10.—DRAWN CARTRIDGE CASE.
A, at the bottom, *B* in the wall, before annealing.   *C*, bottom and *D*, wall after annealing. $\times$ 100.   *E*, unannealed wall ($\times$ 200 through a green filter) shows slip-plane markings in worked metal.

Note in the annealing that the first step is the disappearance of old grain boundaries in the formation of numerous small unstrained crystals, reestablishing a state of equilibrium. There follows a gradual grain growth with continued annealing. As shown in Fig. 10D, this recrystallization was stopped at a point where the grains were still fairly small in order to retain some of the stiffness of the shell wall. For purposes of comparison, a 30-min. anneal at 1100° F. brought section 10B back to equiaxed crystals appreciably larger than those indicated by the old grain boundaries.

Frequency of Annealing

The ductile metals strain-harden with cold working, whether the operation belongs to the rolling, bending, drawing or swaging group. After a certain amount of working, recrystallization is necessary to restore the shattered grain structure and avoid fractures which no annealing will heal.

The rate of strain-hardening and therefore the frequency of recuperative annealings is not the same for every metal, but may be the same for any one metal if plotted against a suitable measure of work done. The problem is one in which the sheet-metal trade is especially in need of metallurgical assistance.

The cartridge shell example is poor commercially in view of the seemingly lavish use of an anneal after every operation. In aluminum, a large factory manufacturing cooking utensils advises that it usually gets three draws between anneals. In 0.10 per cent. carbon steel, we have an example of two severe draws totaling 59 per cent. reduction or the equivalent of 144 per cent. elongation between anneals; but photomicrographs of a sample showed minute fractures in the structure after the second draw. In other cases, there are three to five draws per anneal.

Operating men report that a rapid sequence of draws permits greater reductions between annealings, possibly because a slightly elevated temperature is maintained by friction, internal and external. It is reported that, by putting into a series more operations of less individual severity, a greater total reduction per anneal can be obtained; but all of this still requires too much of "cut and try."

The squeezing group of operations logically follows the drawing group. However, as the two have much in common in their dependence upon "the plastic workability of the metal," occasion is taken here to discuss that interesting subject as a unit.

Rate of Strain-hardening

Figs. 12 to 15 show curves developed from experimental tests on a sample of Tobin bronze rod to demonstrate some tentative ideas on cold

working and the relative rate at which it strain-hardens a metal.   Table 2 brings out some of the same points in tabular form.

The recorded curves, such as the one shown in Fig. 11, which was the original for Fig. 12, were drawn on an Olsen recording testing machine by Mr. Mattera.   The tensile specimens (Fig. 4) were turned up to standard specifications with 0.505-in. body diameter.   Compression specimens began approximately 0.720-in. dia. by 0.645 in. high.   Annealing was performed in an electric furnace at 1100° F. for ½ hr. with cooling in the furnace.   Brinell hardness numbers ranged about 132 as received, 95 annealed and 185 maximum reached in tests.
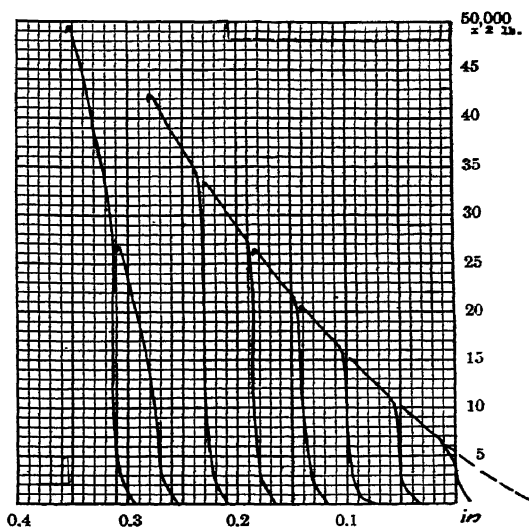
FIG. 11.—ANNEALED TOBIN BRONZE COMPRESSED STEP BY STEP, SHOWING PROGRESSIVELY INCREASING YIELD POINT AS IT IS STRAIN-HARDENED; THEN REANNEALED AND TEST CONTINUED.

The original reason for preparing Fig. 11 was to give a visual demonstration of the progressively increasing yield point, the cumulative effect of strain-hardening.   An annealed slug was squeezed down about 0.050 in., removed, measured, tested for hardness, returned to the machine, squeezed farther, tested again, etc., to about 50 per cent. reduction in height.   Each time the material behaved elastically up to the new yield point, which corresponded to the previous peak.   No signs of fracture had appeared thus far, but the reduced slug (now 0.992-in. dia. by 0.338 in. high) was reannealed and the test resumed.

The second initial yield point was nearly, but not quite, as low as the first, an effect observed also on a similar test on steel.   This may be due to a residual effect, after annealing, of tensile preworking in the first case, and of compressive preworking in the second, or it may be due to differ-

ences in proportions of the blank and an increased pyramiding of resistance toward the center as the blank becomes thinner compared to its diameter. The last reason is also blamed for the somewhat steeper rate of increase of resistance in the second curve after replotting in Fig. 12.

Figs. 13 and 15 show respectively compression and tensile tests of samples both annealed and as received. As explained in connection with Fig. 3, the recorded curves were plotted against unit stress on
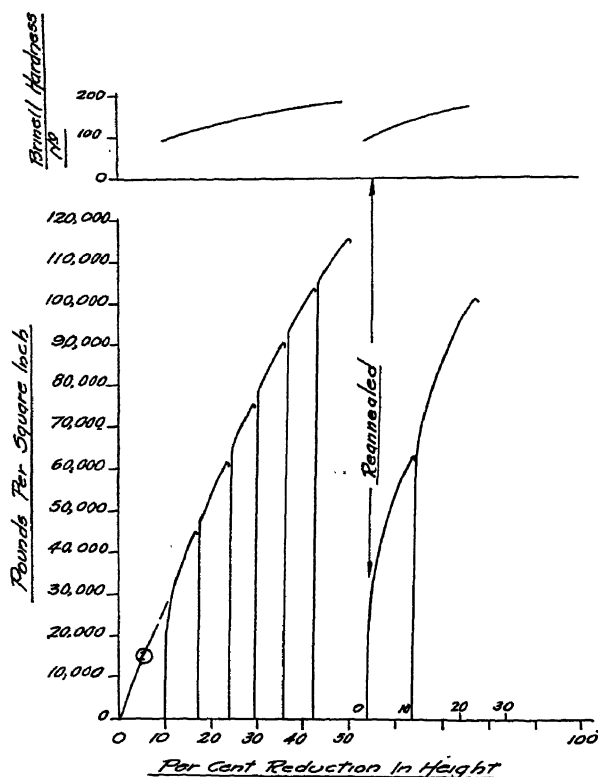
FIG. 12.—FIG. 11 REWORKED TO SHOW UNIT STRESS AGAINST PERCENTAGE REDUCTION. CURVE 1 TRANSPOSED TO SHOW ZERO STRAIN-HARDENING AT ORIGIN.

original cross-section on one coordinate and percentage deformation on the other. These curves were then corrected as shown to give unit stress on the actual cross-section as it changed with the progress of the test.

Constant volume, which is assumed as the basis of conversion, is approximately correct. In the compression test, the given figure, thickness, is divided into the volume, giving a figure for area which is slightly inaccurate on account of some bulging of the sides of the specimens. In the tension test, the given figure is the gage length, 2 in. plus the recorded

extension, up to the point where general elongation ceases and necking begins. The next point is the actual end of the curve at the neck where both load and section area are measurable. (See Fig. 15.)

The relation of *unit* stresses, and of distortions in working metal in opposite directions, that is, in tension and in compression, is of extreme importance to this argument. On the individual slip plane, recrystallization establishes an equilibrium condition. A distortion or slip of a given amount in either direction from this position might properly be
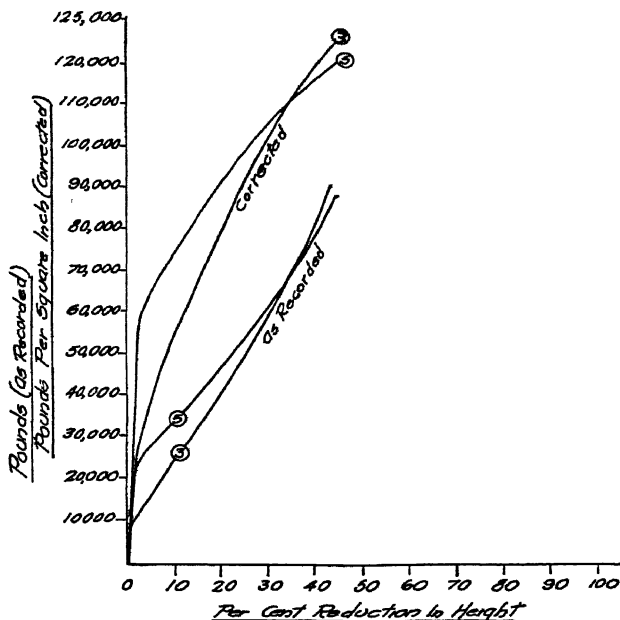
Fig. 13.—Compression tests of Tobin bronze as received and annealed, with relocation to read actual unit stress.

expected to meet with an identical resistance, so far as the individual crystal is concerned.

Change in the length of a rod between 5 and 4 in. might be described either as 25 per cent. elongation or 20 per cent. reduction depending upon direction. Assuming an identical uniform and unstrained structure in each case, the initial yield point or *unit* stress to start movement in either direction should be the same. Then, bearing in mind that the material is (practically) incompressible, and is otherwise unrestrained, the amount of working or strain-hardening which this metal undergoes in movement over the same range, in either direction, should result in a common, though higher, *unit* stress at the end of the movement. *Unit* stress is emphasized for the obvious reason that tensile movement decreases the cross-sectional

area and thereby tends to decrease the *total* stress. Similarly, compressive movement increases the section area and with it the total stress.

If these premises are correct, it should be possible, by using a common measurement for movement, to superimpose tensile and compressive unit stress curves as in Fig. 14.

As suggested by curve 1 in Fig. 12, samples of the same metal which have undergone different amounts of cold working should show plastic stress-strain curves which should fall along a common "rate of strain
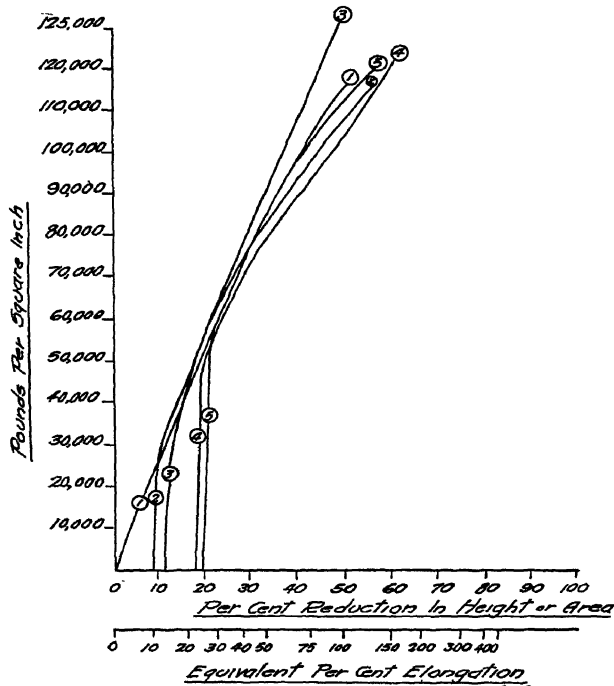
Fig. 14.—Assembly of compression and tension tests of annealed and unannealed Tobin bronze to show common rate of strain-hardening (from Figs. 12, 13 and 15).

hardening" curve. Their starting points on this curve may be indicated by their initial yield points.

In order to establish a zero point, which may possibly be designated as maximum plasticity, the outline of the recorded curve in Fig. 11 was continued down with an imaginary line. This established the zero point in Fig. 12 and gave the initial yield point, as annealed, a strain-hardening rating equal to 10 per cent. reduction.

The outline of curve 1, Fig. 12, was then transferred to Fig. 14 as the basic "rate of strain-hardening curve" for Tobin bronze (at room temperature). On this were plotted the corrected or unit stress curves for the

tensile and compression tests of both annealed and unannealed samples. In doing this, they had to be shifted to suitable starting positions which necessitated a correction of all "per cent. reduction" readings, increasing the steepness of the curves.

Inaccuracies of method may account for discrepancies in alignment. Machine friction and play give inaccuracies in the recorded curves which, in turn, are rarely fine lines.   Vital dimensions cannot always be obtained precisely.   Curves must be replotted and relocated several times with slide rule calculations.   The portion of the tensile curve between the
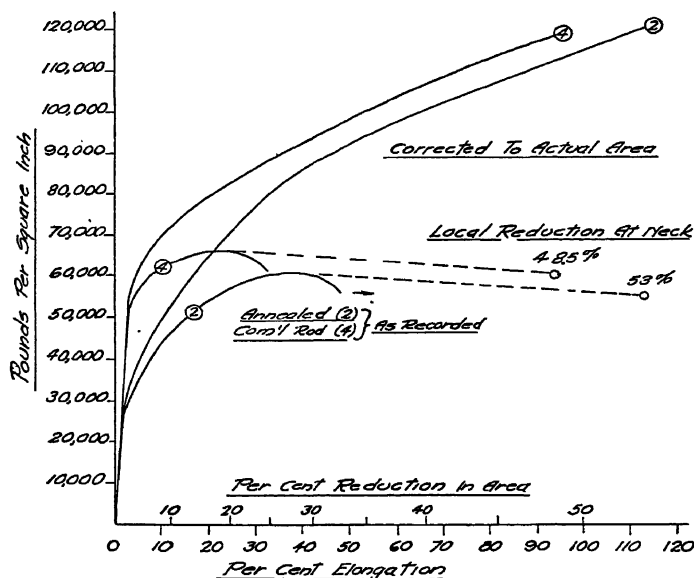
FIG. 15.—TENSILE TEST OF TOBIN BRONZE AS RECEIVED AND ANNEALED, WITH RELO-
CATION TO UNIT STRESS AND PERCENTAGE CHANGE.

end of the general elongation and the neck fracture must be approximated. Nevertheless, the general trend of the curves seems hopeful.

Table 2 groups some of the results of the physical tests.   Note the differences between the actual ultimate tensile strength at the neck and the nominal or common ultimate tensile strength which is not really a unit stress at all.

Note also the difference between general elongation in 2 in. (before necking starts) which varies with the speed of the test, and ultimate elongation at the neck.   This last may be read conveniently from percentage of reduction in area for any tensile test, by means of Fig. 16, which is merely reciprocal logarithmic scales, renumbered to suit ascending and descending percentage changes.   Ultimate elongation and actual ultimate tensile figures are approximate limits for stresses actually occur-

ring in press-working operations. These, if available, with the yield points, tensile or compressive, and the shearing resistance of the material as received would be the items of interest to the press trade.

TABLE 2.—*Properties of Tobin Bronze Rod*

Analysis (Published): Copper, 61.2 Per cent.; Zinc, 37.3.; Tin, 0.9; Lead, 0.4; Iron, 0.2.

Physical Test	Annealed 1100° F. ½ Hr.	As Received
(General) Elongation in 2 in., per cent...............	46	31
(Ultimate) Reduction in area, per cent...............	53	48.5
(Ultimate) Elongation (at neck), per cent............	113	94
(Nominal) "Ultimate tensile," lb. per sq. in	60,500	66,000
Actual ultimate tensile, lb. per sq. in.................	120,000	118,000
(Initial) Yield point:		
Tensile test, lb. per sq. in........................	25,000	52,000
Compression test, lb. per sq. in....................	24,500	59,000
At 20 per cent. reduction = 25 per cent. elongation:		
Tensile test, lb. per sq. in........................	71,000	83,000
Compression test, lb. per sq. in....................	80,000[a]	92,300[a]
(Nominal) Resistance to shearing,[b] lb. per sq. in........	36,400	42,400

[a] Higher on account of pyramiding effect in compression.

[b] Shearing test performed on ¼ × 2-in. Tobin bronze strip.
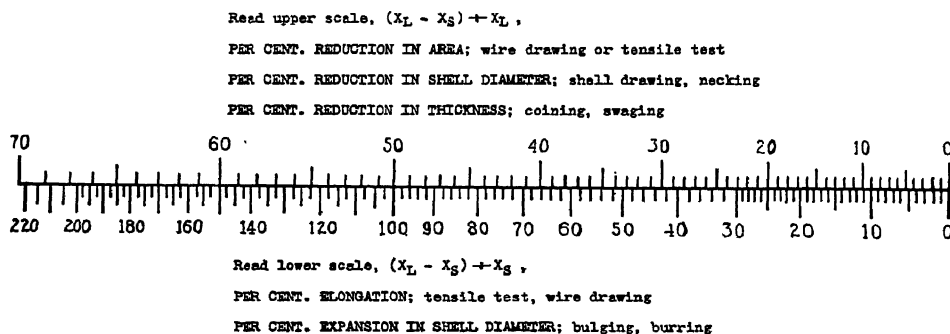
FIG. 16.—RELATION BETWEEN PERCENTAGE OF REDUCTIONS AND OF ELONGATIONS.

SQUEEZING GROUP OPERATIONS

Cold-working operations of the squeezing group strain-harden the metal in proportion to the extent to which it must be moved. Instead of annealed material, many swaging and cold forging operations start with "quarter hard" or "half hard" rolled stock, in order to avoid "dragging down" of high points by tensile stresses. The initial yield

point, as indicated in Fig. 12, is then relatively high and the unit resistance to plastic working continues on up from that point.

The mere surfacing or squeezing to size of forgings and castings usually involves the least metal movement of any of the squeezing operations. The metal being squeezed, if clean and relatively soft, will take the impression of the die surfaces whether they are ground smooth, etched, engraved or sunk to a design or are highly polished. Severe movement, however, is likely to show flow marks even against a smooth die, especially if there is a little oxide on the surface.

Government coinage of the precious metals involves relatively little movement and therefore relatively little strain-hardening. The tool pressure required to fill all die cavities will be increased, however, with any increase in the hardness of the blanks or planchets. This pressure need amount to comparatively little more than the initial yield point of

FIG. 17.—OPERATIONS IN PRODUCTION OF A COLD-FORGED COPPER LEVER, BLANKED AND SWAGED FROM ROLLED STRIP.

the metal as furnished, but with the use of closed dies and a relatively rigid press, a careless set-up may easily cause very high pressures.

The embossing or stamping of emblems, cover designs, hollow knife handles, etc., in thin metal with male and female dies may be arranged, but rarely is, so that the process involves merely drawing, stretching or bending the metal to the profiles of the tools. More often, however, sharp lines required in the design or imperfect allowance of metal thickness clearance requires that the metal shall be actually made to flow at many points. The danger here is that an effort will be made to squeeze over large plane areas where flow is practically impossible, instead of just locally where the sharpness of outline is required.

From the metal-working standpoint, the severest squeezing operation is swaging or cold forging of a plain slug or blank to a finished shape. Of the nonferrous metals, copper is the outstanding example in this group. Many electrical contact points, and arms, nuts, levers, segments, etc., are being cold-forged now, and the art seems to be spreading. It is interesting to note, in this connection, that the hot forging of copper is rather unpopular on account of the erosive action of the hard black

oxide and the narrow range and high temperature at which it is readily forgeable.

At normal room temperatures, both pure electrolytic copper and, to an even greater extent, a lead-bearing copper, are extraordinarily malleable; next, in fact, to gold and silver. Fig. 17 is a good example of a copper forging. The blank is cut from rolled strip to suitable shape. It is then upset in the second step, squeezed edgewise in the third, squeezed sidewise in the fourth, and trimmed in the fifth. No annealing is required, and, as all operations are performed cold, they are relatively cheap. The blank, as in hot-press forging, should be developed or selected to favor the shape as much as possible.
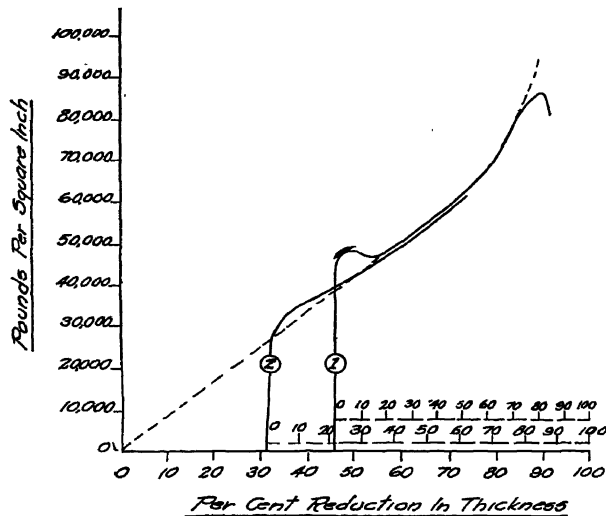
FIG. 18.—RATE OF STRAIN-HARDENING CURVE FOR COPPER IS EXTREMELY LOW. CURVES FROM UNRELATED SPECIMENS.

In Fig. 18, curve 1 is arranged from a cold compression test of slugs of electrolytic copper rod, as received, to indicate tentatively the rate of strain-hardening of such copper. The result is obviously a far more gradual rise than that shown for Tobin bronze in Fig. 14. The original test curve was plotted from over one hundred readings and was then revised to read in unit stress versus percentage reduction in height. The assumption that the rate of strain-hardening curve is a straight line up to the point where it joins the test curve may be somewhat in error, though there are indications that it is not far out.

The hump at the yield point of the test curve is attributed to the fact that the sample was taken from rod which had been severely worked in tension. This would give a relative offset of atoms all one way from the equilibrium position along the individual slip planes. As soon as the

yield point has been passed in compression, the atoms might readily be expected to be moved back along the same slip planes and past the equilibrium position before the resistance begins to rise again.

The hook at the end of the curve was attributed to fractures around the periphery of the slug which had become very thin in proportion to its diameter. The final thin blanks showed measurably greater thickness in the center than at the edges, indicating that a higher local pressure in the center caused a greater deflection there of the hardened steel die blocks. This pyramiding of pressure toward the center of thin blanks has been noted elsewhere, and is attributed to the state of plastic flow which lies between nonfluid elasticity and the fluidity of liquids. Liquid lubricants build up a high pressure in the center of a bearing, due to the thinness of the film with respect to its area and the slowness with which it can escape. At the other extreme, an elastic cylinder built up of a core with shrunk rings about it might be expected to show an increasing pressure toward the center, since compression of the central core requires expansion of the shrunk rings to permit displacement, thereby adding to the normal compressive resistance of the core.

This pyramiding of pressure toward the center of a relatively low compression test slug will naturally yield a proportionately high average unit stress. Accordingly, in a rate of strain-hardening curve (Fig. 14), the compression tests should end higher than the tension tests, which they seem to have done. Also, in Fig. 12, the second curve, obtained with a thinner and broader slug than the first curve, shows a steeper rate of ascent after proper corrections for position have been made.

In order to obtain a check of curve 1 (Fig. 18), a compression test was run upon a slug cut from an old copper contactor, reducing it to 63 per cent. of its original height. The recorded curve was reworked in terms of unit stress and percentage of reduction. This was then located as curve 2 in Fig. 18. The hardness of this sample rose from Brinell No. 65 to No. 107 in the course of the test.

EXTRUSION IN POWER PRESSES

In point of metal working, extrusion is the most severe operation of the squeezing group, and, in fact, of all press operations. Most of the common nonferrous metals in the (commercially) pure state, as well as alpha brass and some white metal alloys, may be made to flow rapidly through small orifices, without preheating (except, perhaps, in the case of zinc).

Considerable heat is evolved in the process, a point also noted, though to a lesser extent, in all other metal-working operations. In extrusion, the heat generated is the principal factor limiting speed of operation, although it is also of value in reducing tool loads, as the rate of strain-hardening is generally less at the higher temperatures. In shearing

operations conducted at relatively high speeds, the heat generated is occasionally considered detrimental to the tools. In drawing operations performed in a consecutive series, the resultant warmth should retard strain-hardening to some extent and therefore be looked upon favorably.

Incidentally, could we not consider this heat evolved in cold working and its counterpart, the heat delivered to raise electrons to an activity at which recrystallization takes place, as a latent heat of recrystallization? This would probably not be a constant amount of heat, as in the case of fusion and vaporization, because of the wide variation possible in the amount the metal may be strain-hardened.

To return to extrusion, in Fig. 19 sketch A illustrates the more severe of the two common methods. Squeezing the bottom of a shell to force metal there to flow up around the punch requires greater unit stresses than does squeezing a thick side wall vertically to flow the metal down into a thinner wall, as in sketch B. The explanation is that in method A much of the metal must move a greater distance to reach the orifice than in method B, and also that the pressure tends to pyramid in the center as the blank becomes thin in proportion to its diameter.
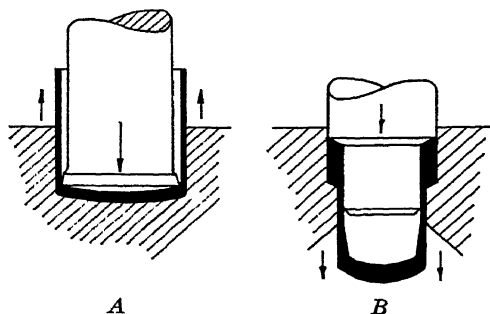
FIG. 19.—POWER-PRESS EXTRUSION.
A, moving metal from bottom; B, moving it from wall (the least severe).

This difference in severity is borne out by the fact that method A, which permits the use of a simple blanked slug, is used for the softer metals, while method B, which requires two or three operations and anneals to prepare the slug, is used especially for copper and brass.

Fig. 20 shows a typical group of extrusion samples in which parts 1, 2, 3, 4 and 6 are produced by method A, with some modifications of bottom shape, from lead, zinc, tin and aluminum (4 and 6) respectively. A modification of method B, known as the Hooker process, which includes a method of trimming, is used to produce parts 5, 7 and 12 from 70:30 brass, pure aluminum and pure copper respectively. The small parts, 8 to 11, in tin, lead and zinc, employ modifications of both methods.

Tin, lead and zinc crystallize in lattice patterns which are not favorable to cold working, but, as tin and lead recrystallize below room temperature, at which they are worked, and zinc below 300° or 400° F., at which it is usually extruded, they are all really in their hot-working range. Aluminum and brass show distinctly the effects of severe cold working, and must be annealed both before and after the extrusion operation if

ductility is required.   Foisy[4] claims that copper comes from the long extrusion, shown at 12 in Fig. 20, in practically an annealed state.   This may be due both to the extremely low rate of strain-hardening for copper, and to a very high operating temperature resulting from fast operation and a long extrusion.

Fig. 21 shows a micrographic study of the extruded 70:30 brass cartridge case shown at 5 in Fig. 20, which is of the same size as the drawn case shown in Fig. 8.   This is especially interesting because it
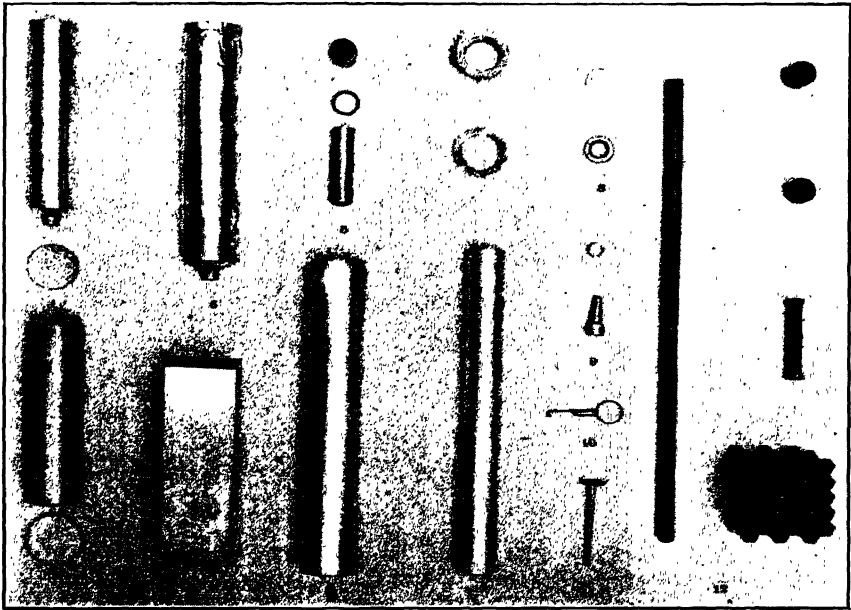
FIG. 20.—SAMPLES EXTRUDED BY METHOD A FROM TIN, LEAD, ZINC AND ALUMINUM; AND BY METHOD B FROM BRASS, ALUMINUM AND COPPER.

affords a comparison of extruded structure with that of the drawn shell, Fig. 10.   The details of treatments of the samples are the same as before. The photomicrographs A and C were taken at the bottom of the shell, point 1, Fig. 9, before and after annealing, respectively; B and D were taken near point 3 toward the top of the wall section before and after annealing.

The strain-hardened side wall B is the most interesting, of course. After working, which amounts to an elongation, of, say, 600 per cent., it shows a uniform structure without evidence of overstrain fractures.

[4] G. A. Foisy: The Manufacture and Application of Extruded Copper Tubes. *Trans.* Amer. Soc. Mech. Engrs. (1927) **M.S.P.-50-9**, 93.

Old grain boundaries could not be developed, except that the dark and light streaks down the center seemed certainly to be much elongated dark and light crystals. This structure merged quite quickly at the bottom corner (point 2, Fig. 9) into large old grains showing numerous strain lines and then into the largely unstrained structure shown at A.
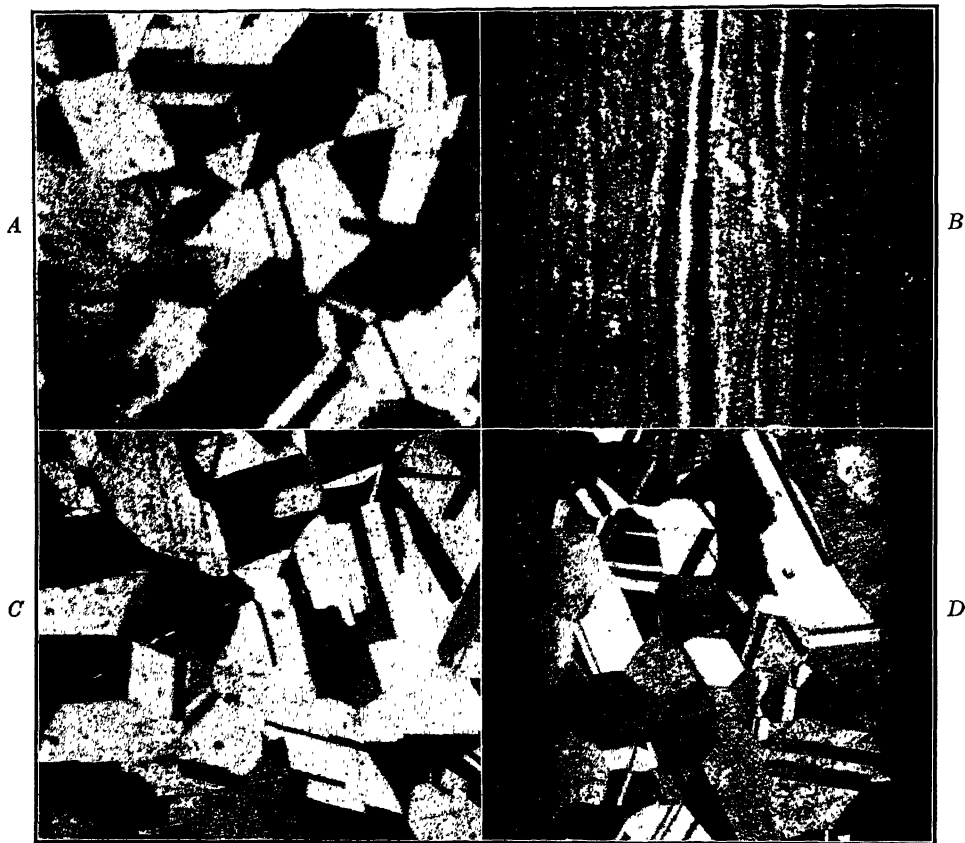
FIG. 21.—EXTRUDED CARTRIDGE CASE. × 100.

A, at bottom and B, the wall as extruded; C, the bottom and D, the wall after annealing.

An anneal of 7 to 8 min. at 1300° F. changed the extruded structure B to the equiaxed unstrained structure D without apparent evidence of residual directional properties. A larger annealed crystal size resulted after extrusion than after drawing with an identical anneal. The explanation would be that the much more severely worked material began to anneal at a much lower temperature, permitting a greater growth in the time allowed.

It is interesting to note that work is being done by several investigators on a method of extruding cast slugs, on the theory that the refinement of the cast structure is ample in itself without the preliminary refinement of rolling. On the side of economics, the cost of casting, cropping and cleaning many small blanks must be set against the quantity production method of rolling a billet and cutting the blanks in multiple in fast automatic presses.

Hot-press Forging

The last classification under the squeezing group of press operations, and really the only important group involving elevated temperatures, is hot-press forging. Of the nonferrous metals, by far the greatest interest is in beta brass, although duralumin, copper, aluminum bronze, aluminum and zinc are also press-forged to some extent.

2000
1800
1600
1400
1200
1000
800
600
400
200
0
Degrees Farenheit
0
10
20
30
40
50
60
70
80
90
100
Per Cent Reduction In Thickness (Unit Blow)
Copper
70-30 Brass (α)
60-40 Brass (β)
Aluminum
Zinc
Tin
Lead
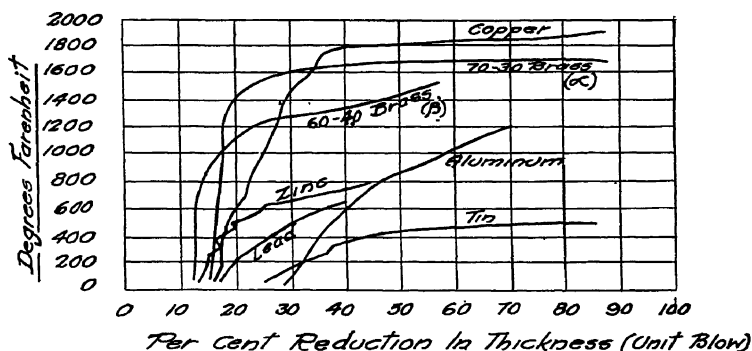
Fig. 22.—Forgeability of metals under a unit blow shows changes in rate of strain-hardening and shows forging ranges. (W. L. Kent.)

Fig. 22 is a group of extremely interesting curves obtained by W. L. Kent[5] in a series of experiments in which he dropped a weight a uniform distance (50 ft-lb.) upon slugs of several metals, ½ in. in diameter by ½ in. high, heated to different temperatures, and took the percentage deformation as a measure of forgeability.

Note, for example, that 70:30 alpha brass does not change appreciably from its malleability when cold until it reaches a point where the change is sudden and the resultant forging range of temperature is narrow. In copper, the increase in malleability, or decrease in rate of strain-hardening, is gradual up to an even more sudden point of change and an equally narrow forging range.

The beta brass curve, on the contrary, breaks rather gradually and gives a lower and wider range for forging. The curve checks well

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[5] W. L. Kent: The Behaviour of Metals and Alloys During Hot Forging. *Jnl.* Inst. Metals (1928) **39**, 209.

with practice, as most firms specify 1250° to 1400° F. for (beta) brass forgings and occasionally go as low as 1150° F. when the dies are thoroughly heated.

Speed of operation has considerable effect both upon strain-hardening and upon restoration of structure and there is much we would like to know about it. In cold working at normal testing and working speeds, metal movement is transcrystalline, and loads and most test results are unaffected by change of speed (except general elongation before necking). Above the recrystallization temperatures, it is possible to get intercrystalline movement at moderately low speeds. At normal rolling[6] and press-forging speeds, however, change of speed does not affect mechanical resistance appreciably, so that the movement probably is all transcrystalline and strain-hardening takes place in some inverse proportion to the temperature. In this case, it seems that corrective annealing takes place apparently spontaneously but more likely at a rate depending upon the time taken in working the metal and the surplus heat available for recrystallization. In this connection, note Table 3 and Fig. 24.

Table 3, from the data obtained by Mr. Kent, shows the hardness of copper after hot working at different temperatures and after cold working

TABLE 3.—*Comparison of the Hardness of Copper after Hot Working, Cold Working and Annealing*

Brinell Hardness Numbers			Forging Temperatures	
A Cold-worked[a]	B Annealed[b]	C Hot-worked[c]	Deg. C.	Deg. F. (app.)
76	77–70.5	68.6	300	575
75.8	43.8	67.	450	850
77.5	42.4	66.9	550	1025
79	43.9	58–46.7	600	1100
80.3	42.9	42.6	650	1200
81.3	42.9	44.6	700	1300
83	42.7	44.5	850	1550

[a] Cold-worked to same reduction as C.
[b] Cold-worked samples annealed 10 min. at 300° C.
[c] Hot-worked under 50 ft.-lb. blow.

by similar amounts. At 575° to 1025° F., the annealing that takes place during forging and after it, due to the heat in the small slug, was not enough to correct the strain-hardening, although the resultant hardness was not nearly so great as was produced in cold working. Above 1100° F., however, the annealing seemed to be spontaneous, as the hot-worked slugs were as soft as corresponding annealed, cold-worked slugs.

[6] W. Trinks: Roll Pass Design, II. *Rolling Mill Jnl.* (1929) **3**, 67.

Fig. 23 shows a photograph of the cross-section of the brass forging shown at 7 in Fig. 25. This forging was produced from a cylindrical slug of about one-third the final diameter, in a press that was too slow in action
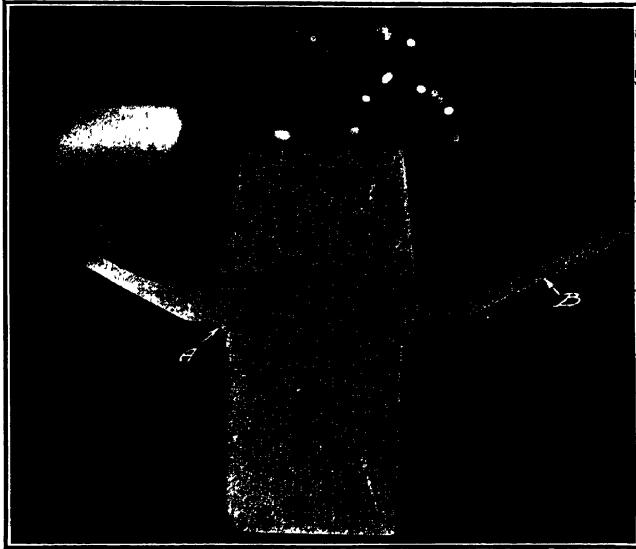
FIG. 23.—CROSS-SECTION OF BRASS FORGING (LARGELY BETA) SHOWN AT 7 IN FIG. 25.
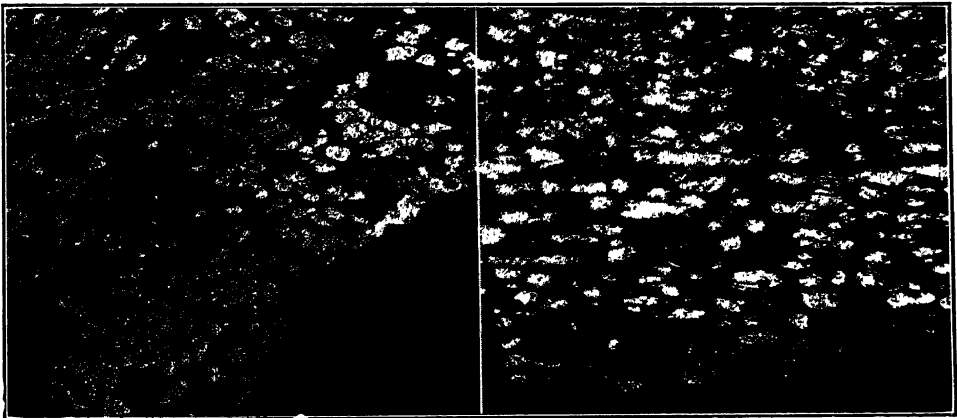
A   B

FIG. 24.—PHOTOMICROGRAPHS AT POINTS A AND B, FIG. 23. × 180.
Showing elongated crystals near the surface, indicating flow.

for such a small piece, so that there was a tendency to chilling on the outer face. Unstrained but much elongated grains are found in the heavy

area where the flow lines show and along the outer face of the shell. Smaller equiaxed grains fill the heart of the forging, and the remainder of the shell web.

This is shown in some detail in Fig. 24. The number of white alpha crystals would mark it as being below the all-beta boundary, at least in the cold state. Note the elongated crystals tending to follow the profile of the forging a little below the surface. Fig. 24*A* was taken in the corner where the wall begins, while Fig. 24*B* was taken part way out along the wall. It shows the tendency to smaller crystals in the heart of the thin sections.

The metal is worked in this forging as in most others, relatively little in the heavy portions and severely in the thin portions and the flash.
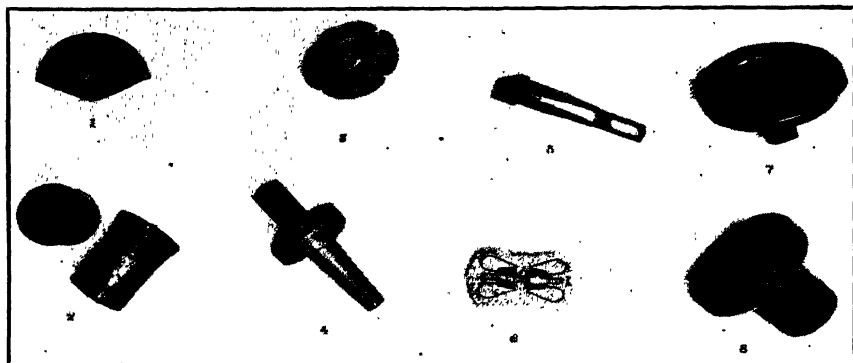
FIG. 25.—TYPICAL GROUP OF BETA BRASS PRESS FORGINGS (PART 2 IS STEEL).

The amount of working may be controlled to a considerable extent by proper selection of the shape of the slug. Here, as in extrusion, the idea of eliminating the more or less unnecessary preparatory refinement of rolling is rather tempting, with the added advantage that it may be possible to run the hot cast slug directly to the forging operation with little or no additional heating. While there are obvious difficulties in this process, it is said to have been worked out commercially in the ferrous field in at least one instance.

ACKNOWLEDGMENTS

DISCUSSION

(J. L. Christie presiding)

C. F. HAMMOND, New Haven, Conn. (written discussion).—On page 296, last paragraph, Mr. Crane says, "Fig. 10E, taken through a green filter, shows more clearly than 10B the numerous (parallel) slip planes which mark the movement and break up the old crystals into many tiny fragments." This statement may be misleading and convey the wrong impression. The grains in photomicrograph 10E are not ruptured or broken up into tiny fragments. The slip bands are merely planes of slippage, the original grains remaining intact. This is characteristic of cold-worked brass or other metals.

On page 298, Mr. Crane says, "The cartridge shell is poor commercially in view of the seemingly lavish use of an anneal after every operation." I do not agree that cartridge manufacturers use too frequent anneals after each drawing operation. It may not be well known, but cartridge cases are manufactured, at least by the Winchester Repeating Arms Co., to a definite microstructure. The draw layout and tools are made to produce this structure. This is necessary to produce the maximum strength and prevent such difficulties during explosion as bursts, partial and complete separations of the shell and numerous other defects. We also find that anneals after drawing operations are necessary as a matter of tool economy. Attempting to overwork the metal would cause considerable tool breakage in view of the delicate tools used in cartridge manufacture. These tools are very expensive, consequently tool cost is an important item. It is, of course, natural that attempts have been made to reduce the number of anneals between drawing operations and invariably the punch pushes through the bottom of the shell. This condition, of course, is not experienced in extruded cartridge cases, as the metal is squeezed through an orifice between the punch and the extrusion bushing, thereby allowing in one operation a much longer shell than by the punch-and-die method.

Cartridge manufacture naturally is a specialized art. The one fact that is always considered is the safety of the ammunition to the user. This is an additional reason why the metal in cartridge cases is not stressed during manufacture to the danger point of causing incipient cracks or ruptures, which may cause bursts in the finished loaded shell during the act of firing. In most press metal operations the blanking and forming of the metal can very well approach the point of producing incipient cracks and minor ruptures without causing difficulty.

E. V. CRANE (written discussion).—It was certainly not intended to suggest that the breaking up of the continuity of the old crystals had been carried so far that actual fractures had begun to appear. These, of course, cannot be removed by annealing as can the distortions occasioned by slip-plane movements.

It would be equally erroneous, however, to imply that the area enclosed by the old crystal boundary still represented an uninterrupted crystal pattern. The (small) increase in volume accompanying cold working indicates that distances between atoms have been increased in many places, even though not to the extent of completely breaking the force of attraction between them. By definition, the equilibrium relations between layers of atoms have been destroyed along every slip plane traversing the crystal. An indication of the extent of the damage is evidenced when sufficient heat is applied to the cold-worked material to permit the atoms to rotate into less strained positions. The old grain boundaries are lost at once and the equilibrium condition emerges as a great number of very small crystals. These gradually realign into larger and larger crystals until the metal is restored to a state equal to that before the plastic working occurred.

The writer's use of cartridge cases as an example to illustrate changing structure in plastic working, and subsequent criticism of them as an economical example of what might be termed the plastic cycle, was not intended as a criticism of cartridge manufacturing processes. If one anneal were eliminated it would be at the expense of at least one more drawing operation, with other contingent problems as suggested by Mr. Hammond. A discussion of it would be too special and too extensive to enter into here.

There is a distinct need, however, for strain-hardening curves for all metals subject to plastic working. The lower limit for each curve would be the commercially annealed state of the metal, and the upper limit the point at which all available slip planes have been used up and internal fractures are likely to start. Such curves show the amount of cold working expressed as percentage of reduction in diameter or thickness, etc., which might be accomplished between anneals. The writer is preparing a more thorough discussion of this subject for publication in book form.

Forming Properties of Thin Sheets of Some Nonferrous Metals

By W. A. Straw,* M. D. Helfrick† and C. R. Fischrupp,† Chicago, Ill.

In the manufacture of telephone apparatus a number of nonferrous sheet metals are blanked and formed to produce a wide variety of parts, which are generally small in size because of space and weight requirements. Many are given sharp bends in forming, so that they may be assembled into compact units. This study covered sheet metal of the alloys of brass, phosphor bronze and nickel silver that are most extensively used by our company. In general, the sheets range from 0.005 to 0.100 in. in thickness and from $\frac{1}{4}$ hard to extra spring temper in hardness. As many parts function as flat springs, and others require the maximum stiffness for structural reasons, a large percentage of the metal is used in the hard and spring tempers. So, because of the necessity for the minimum radius of bend consistent with the maximum in hardness, there has been a need for information as to the forming characteristics of these sheet metals in the various alloys, tempers and thicknesses. The literature yields relatively little regarding such forming characteristics, so that designers of apparatus and tools have been largely dependent upon past experience or tool tryouts for guidance.

In presenting tabular data intended as a basis for selecting the temper of the metal and radius of the bend, we recognize the influence of many other factors which are not covered in this study. For example, the angle of the bend and conditions of the metal, such as grain size and presence of impurities, as well as conditions of the fabricating process, such as rate of forming and adjustment of the tools, may all affect the result. In addition, a bumping operation subsequent to forming, which is frequently used to set the bend, increases the strain on the metal.

We wish to emphasize the fact that this is not considered a scientific investigation of the formability of materials or an attempt to correlate forming characteristics with various other properties of the metals, except in so far as such properties are controlled by commercial limits on composition and temper.

It is expected, however, that the data presented may serve some useful purpose in estimating the relative formability of different thicknesses

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† Engineer, Western Electric Co., Inc.

and tempers of the commonly used alloys included in this study. Allowance must be made, in any specific use of the data, for commercial variations in the metal or in the fabricating process.

MATERIALS STUDIED

Alloys 1 and 2, brass sheet, are commercially known as "high brass" and "clock brass," respectively. Alloy 3 is a leaded brass sheet adapted to moderate forming and machining. Alloys 4 and 5, nickel-silver sheet, contain 72 and 55 per cent. copper, respectively, and each contains 18 per cent. nickel. Alloys 6 and 7, phosphor-bronze sheet, contain 4 and 8 per cent. tin, respectively. The sheets tested were taken from commercial lots conforming to the limits of composition shown in Table 1. The Rockwell hardness values of the specimens tested are given in Tables 2 to 5, inclusive, in connection with the statement of the results obtained. The materials used conformed to the tensile strength and Rockwell hardness limits developed in a recent study of the physical properties of these alloys by Townsend, Straw and Davis.[1]

The selection of the tempers and thicknesses to be studied in each alloy was governed by the use of that alloy in telephone apparatus. Alloy 1, high-brass sheet hard temper, being extensively used, was examined in 14 thicknesses, ranging from Nos. 8 to 30 B. & S. gage, whereas alloy 4, nickel-silver sheet hard temper, since it is not used extensively, was tested in only four thicknesses.

TESTING PROCEDURE

Test specimens, $\frac{3}{4}$ in. wide by 3 in. long, were sheared from sheets 6 or 12 in. wide in three different directions—parallel, perpendicular and at a 45° angle to the direction of rolling. Sufficient specimens from each direction were prepared from the metals of each thickness and temper to permit two forming tests with each of six tools having different radii.

The forming of the specimens was done on a No. 2, 12-ton Bliss press, operated at 148 r.p.m., the length of the stroke being $\frac{1}{2}$ in. Six accurately ground 90° V-shape forming punches were used. One was ground sharp and the others were ground with radii of 0.0156, 0.0312, 0.0625, 0.0937 and 0.125 in., the accuracy of the radii being checked by the use of a Bausch & Lomb contour projector. The die had a sharp 90° groove. Fig. 1 shows the set-up of punch and die and Fig. 2, the various punches.

In forming the specimens neither end was clamped. The distance between the punch and die at the end of the downstroke was adjusted

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[1] J. R. Townsend, W. A. Straw and C. H. Davis: Physical Properties and Methods of Test for Some Sheet Non-Ferrous Metals. *Proc.* Amer. Soc. Test. Mat. (1929) **29**, Pt. II, 381.

to approximately the thickness of the specimen to be formed. The
enclosed angle of the specimen produced in this way was greater or less

TABLE 1.—*Chemical Composition Limits and Nominal Composition for Nonferrous Metal Sheet*

		Alloy 1, or High Brass	Alloy 2, or Clock Brass	Alloy 3, Brass	Alloy 4, Nickel Silver	Alloy 5, Nickel Silver	Alloy 6, Phosphor Bronze	Alloy 7, Phosphor Bronze
Copper, per cent...	nominal	66.00	62.50	65.50	72.00	55.00	95.70	92.00
	minimum	64.50	61.00	64.00	70.50	53.50	94.40	91.00
	maximum	67.50	64.00	67.00	73.50	56.50		
Lead, per cent...	nominal		1.62	0.95				
	minimum		1.25	0.80				
	maximum	0.30	2.00	1.10		0.10	0.05	0.02
Iron, per cent...	maximum	0.05	0.06	0.08	0.35	0.35	0.10	0.10
Zinc, per cent...	nominal				10.00	27.00		
	minimum	Remainder	Remainder	Remainder	8.50	25.50		
	maximum	Remainder	Remainder	Remainder	11.50	28.50	0.30	0.20
Nickel, per cent...	nominal				18.00	18.00		
	minimum				16.50	16.50		
	maximum				19.50	19.50		
Manganese, per cent...	maximum					0.50		
Tin, per cent...	nominal						4.30	8.00
	minimum						3.80	7.50
	maximum						4.80	8.50
Phosphorus, per cent..	nominal						0.20	0.15
	minimum						0.05	0.05
	maximum						0.35	0.25
Antimony, per cent...	maximum						0.01	0.01
Other Impurities, per cent...	maximum	0.10	0.10	0.10			trace	trace

than 90°, depending on the temper and thickness of the metal. In commercial forming, of course, it is customary to use tools of different

angles to produce exact 90° bends or, as previously mentioned, to bump the parts sufficiently to "set" the bend. As either of these methods would introduce a variable, neither was used in this study.
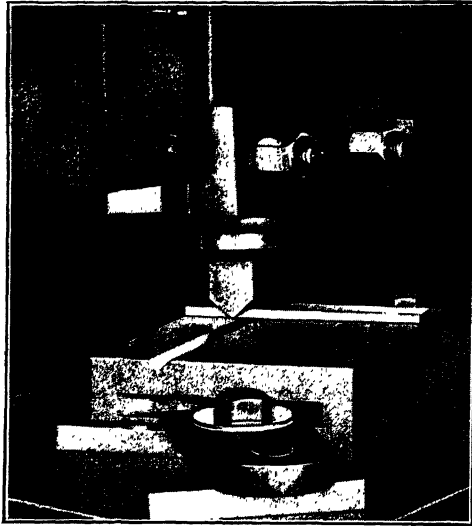
FIG. 1.—SET-UP OF PUNCH AND DIE.

After forming, the specimens were visually examined and classified according to the condition of the outside surface at the bend. The results ranged from complete fractures to bends having smooth surfaces with no
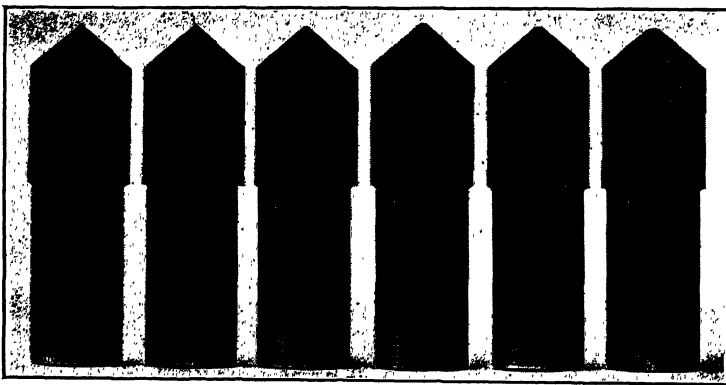
FIG. 2.—PUNCHES.

apparent effect. Intermediate conditions existed, as illustrated in Fig. 3. An arbitrary selection was made of the acceptable condition illustrated by sample 7. In this specimen the surface shows the "orange peel"

condition but no parting or failure is evident.   In Tables 2 to 5, inclusive, the results are summarized by indicating the smallest radius punch that formed an acceptable bend.
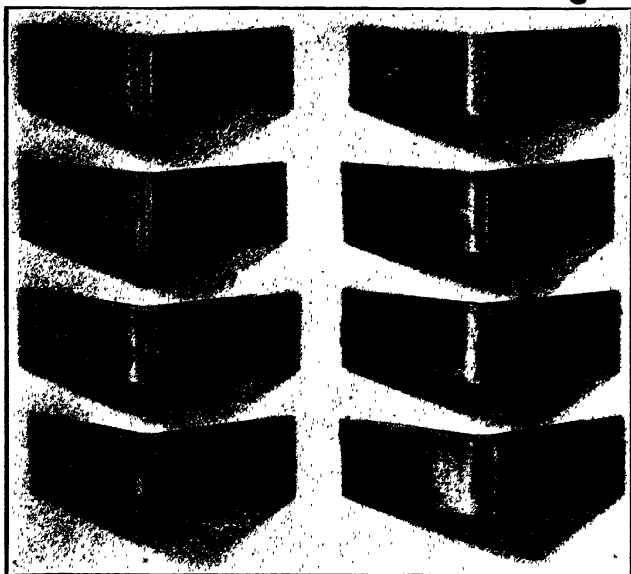
FIG. 3.—FORMED SPECIMENS.
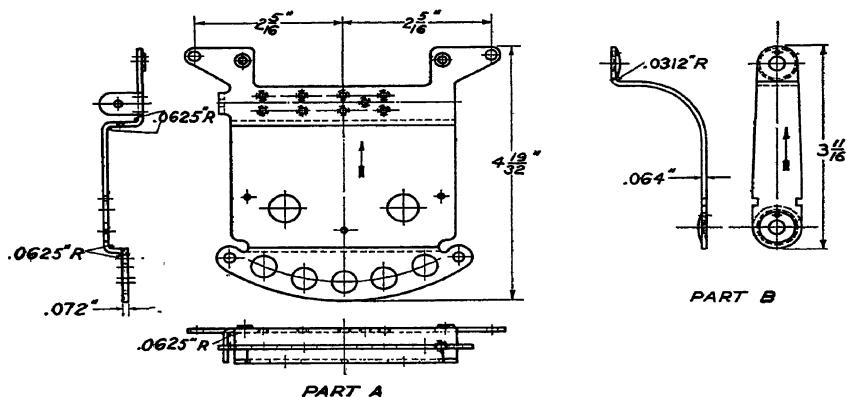
FIG. 4.—PARTS THAT ILLUSTRATE USE OF DATA OBTAINED.
Arrows indicate direction of rolling of metal.

The personal factor in classifying the specimens as to the condition of the bend was largely eliminated by the use of a standard for comparison. It is understood, of course, that a difference of opinion might exist in the

TABLE 2.—*High-brass Sheet, Alloy 1*

Temper, B. & S. Numbers Hard		Thickness		Rockwell Hardness ($\frac{1}{16}$-in Ball × 100-kg. Load × Red Figures)	Minimum Suitable Radius of Punch		
		B. & S. Gage	Inches		Bend Perpendicular to Direction of Rolling	Bend 45° to Direction of Rolling	Bend Parallel to Direction of Rolling
½ Hard	2	20	0.0319	67	Sharp	Sharp	Sharp
		18	0.0403	66	Sharp	Sharp	Sharp
		15	0.0571	68	Sharp	Sharp	Sharp
		14	0.0641	70	Sharp	Sharp	Sharp
		11	0.0907	73	Sharp	Sharp	Sharp
¾ Hard	3	24	0.0201	67	Sharp	Sharp	Sharp
		20	0.0319	71	Sharp	Sharp	Sharp
		16	0.0508	78	Sharp	Sharp	0.0156″
		14	0.0641	78	0.0156″	0.0156″	0.0312″
		11	0.0907	77	0.0156″	0.0312″	0.0937″
Hard	4	30	0.0100		Sharp	Sharp	Sharp
		24	0.0201	76	Sharp	Sharp	Sharp
		22	0.0253	79	Sharp	Sharp	Sharp
		20	0.0319	80	Sharp	Sharp	0.0156″
		18	0.0403	82	Sharp	Sharp	0.0312″
		17	0.0451	83	Sharp	0.0156″	0.0625″
		16	0.0508	84	Sharp	0.0156″	0.0937″
		15	0.0571	83	0.0156″	0.0312″	0.0937″
		14	0.0641	82	0.0312″	0.0312″	0.0937″
		12	0.0808	82	0.0312″	0.0625″	0.0937″
		11	0.0907	84	0.0937″	0.1250″	a
		10	0.1019	81	a	a	a
		9	0.1144	84	a	a	a
			0.1250	80	a	a	a
Extra Hard	6	24	0.0201	83	0.0156″	0.0312″	0.0937″
		20	0.0319	85	0.0312″	0.0625″	a
		19	0.0359	87	0.0625″	0.0937″	a
		18	0.0403	87	0.0625″	0.1250″	a
		17	0.0451	88	0.0625″	0.1250″	a
		16	0.0508	88	0.0625″	0.1250″	a
		15	0.0571	88	0.0937″	a	a
		14	0.0641	89	0.1250″	a	a
		13	0.0719	89	0.1250″	a	a
		11	0.0907	87	a	a	a
Spring	8	30	0.0100		Sharp	0.0156″	0.0937″
		26	0.0159		0.0156″	0.0625″	a
		24	0.0201	88	0.0312″	0.0937″	a
		22	0.0253	90	0.0312″	a	a
		20	0.0319	88	0.0312″	a	a
		18	0.0403	92	0.0625″	a	a
		16	0.0508	90	0.0937″	a	a
		14	0.0641	92	0.1250″	a	a

a None of the radii tested were suitable.

TABLE 3.—*Clock-brass Sheet, Alloy 2 and Leaded Brass Sheet, Alloy 3*

Temper, B. & S. Numbers Hard		Thickness		Rockwell Hardness (⅛ s-in. Ball × 100-kg. Load × Red Figures)	Minimum Suitable Radius of Punch		
		B. & S. Gage	Inches		Bend Perpendicular to Direction of Rolling	Bend 45° to Direction of Rolling	Bend Parallel to Direction of Rolling
ALLOY 2							
½ Hard	2	11	0.0907	71	0.0625″	0.0937″	0.0937″
Hard	4	24	0.0201	76	Sharp	0.0312″	0.0625″
		22	0.0253	81	0.0312″	0.0625″	0.0937″
		20	0.0319	80	0.0312″	0.0625″	0.0937″
		19	0.0359	83	0.0625″	0.0937″	a
		17	0.0451	80	0.0625″	0.0937″	a
		16	0.0508	84	0.0625″	0.0937″	a
		14	0.0641	82	0.0937″	0.1250″	a
		13	0.0719	83	0.1250″	a	a
		12	0.0808	82	0.1250″	a	a
		10	0.1019	78	a	a	a
		9	0.1144	81	a	a	a
			0.1250	79	a	a	a
Spring	8	24	0.0201	87	0.0625″	a	a
ALLOY 3							
¼ Hard	1	14	0.0641	59	Sharp	Sharp	Sharp
½ Hard	2	18	0.0403	63	Sharp	Sharp	Sharp
		16	0.0508	71	Sharp	0.0156″	0.0312″
		14	0.0641	65	Sharp	0.0156″	0.0312″
		12	0.0808	71	0.0625″	0.0625″	0.0937″

a None of the radii tested were suitable.

selection of such a standard. The surface of a part suitable for plating without polishing, for example, would necessitate a different standard from that for parts where strength was the principal consideration.

USE OF DATA

The parts shown in Fig. 4 illustrate the use of the data obtained. For example, part *A*, originally designed to be made from hard temper high-brass sheet, has a lug formed with a maximum permissible radius of 0.0625 in. In order to keep the amount of skeleton scrap as low as possible, it was planned to blank this part in such a way that the bend made in forming the lug would be in the direction of rolling of the metal. Reference to Table 2 shows that a suitable radius for such a bend of hard temper material, parallel to the direction of rolling of the metal, would be 0.0937 in., while if ¾ hard temper material were used the

TABLE 4.—*Nickel-silver Sheet*

Temper, B. & S. Numbers Hard		Thickness		Rockwell Hardness (1/16-in. Ball × 150-kg. Load × Red Figures)	Minimum Suitable Radius of Punch		
		B. & S. Gage	Inches		Bend Perpendicular to Direction of Rolling	Bend 45° to Direction of Rolling	Bend Parallel to Direction of Rolling
ALLOY 4							
½ Hard	2	20	0.0319	48	Sharp	Sharp	Sharp
		19	0.0359	47	Sharp	Sharp	Sharp
		18	0.0403	52	0.0156″	0.0156″	0.0312″
		14	0.0641	51	0.0625″	0.0625″	0.0937″
		13	0.0719	48	0.0937″	0.0937″	0.0937″
		11	0.0907	53	0.0937″	0.0937″	0.1250″
Hard	4	24	0.0201	47	Sharp	Sharp	0.0156″
		16	0.0508	57	0.0625″	0.0625″	0.0937″
		15	0.0571	59	0.0937″	0.0937″	0.1250″
		10	0.1019	61	0.1250″	0.1250″	a
ALLOY 5							
½ Hard	2	24	0.0201	59	Sharp	Sharp	Sharp
		20	0.0319	62	Sharp	Sharp	Sharp
		18	0.0403	65	0.0625″	0.0625″	0.0625″
		16	0.0508	70	0.0625″	0.0625″	0.0625″
		15	0.0571	70	0.0625″	0.0625″	0.0937″
		14	0.0641	66	0.0625″	0.0625″	0.0937″
		9	0.1144	69	0.1250″	0.1250″	a
			0.1250	67	a	a	a
Hard	4	30	0.0100		Sharp	Sharp	0.0156″
		24	0.0201	71	0.0312″	0.0312″	0.0937″
		20	0.0319	70	0.0625″	0.0625″	0.0937″
		17	0.0452	73	0.0625″	0.0625″	0.0937″
		14	0.0641	73	0.0937″	0.0937″	a
		11	0.0907	74	a	a	a
Extra Hard	6	36	0.0050		Sharp	Sharp	Sharp
		30	0.0100		0.0156″	0.0156″	0.0156″
		28	0.0126	67	0.0156″	0.0156″	0.0156″
		27	0.0142	69	0.0156″	0.0156″	0.0312″
		26	0.0159	73	0.0312″	0.0625″	0.1250″
		25	0.0179	76	0.0312″	0.0625″	0.1250″
		22	0.0253	78	0.0937″	0.0937″	0.1250″
		20	0.0319	76	0.0937″	0.0937″	a
		19	0.0359	79	0.1250″	0.1250″	a
		18	0.0403	82	0.1250″	a	a
		16	0.0508	79	0.1250″	a	a
		14	0.0641	80	a	a	a

a None of the radii tested were suitable.

TABLE 5.—*Phosphor-bronze Sheet*

Temper, B. & S. Numbers Hard		Thickness		Rockwell Hardness (⅛ e-in. Ball × 150-kg. Load × Red Figures)	Minimum Suitable Radius of Punch		
		B. & S. Gage	Inches		Bend Perpendicular to Direction of Rolling	Bend 45° to Direction of Rolling	Bend Parallel to Direction of Rolling
ALLOY 6							
½ Hard	2	24	0.0201	26	Sharp	Sharp	Sharp
		20	0.0319	38	Sharp	Sharp	Sharp
		14	0.0641	37	Sharp	Sharp	Sharp
		13	0.0719	42	Sharp	Sharp	Sharp
		12	0.0808	47	0.0625''	0.0625''	0.0625''
		11	0.0907	42	0.0625''	0.0625''	0.0625''
			0.1250	42	0.0937''	0.0937''	0.0937''
Hard	4	24	0.0201	59	Sharp	0.0312''	0.0625''
		20	0.0319	64	0.0156''	0.0625''	0.1250''
		18	0.0403	59	0.0625''	0.0625''	0.1250''
		16	0.0508	66	0.0625''	0.0937''	a
Extra Hard	6	17	0.0453	69	0.0625''	0.1250''	a
Spring	8	28	0.0126		Sharp	0.0625''	a
		27	0.0140		Sharp	0.0625''	a
		26	0.0159		0.0156''	0.0937''	a
		25	0.0179		0.0312''	0.1250''	a
		23	0.0226	72	0.0312''	0.1250''	a
		22	0.0253	72	0.0312''	0.1250''	a
		21	0.0285	67	0.0625''	a	a
		20	0.0139	71	0.0625''	a	a
		18	0.0403	74	0.0937''	a	a
		17	0.0452	75	0.0937''	a	a
		16	0.0508	75	0.0937''	a	a
		14	0.0641	74	0.1250''	a	a
		11	0.0907	73	a	a	a
ALLOY 7							
½ Hard	2	25	0.0179	61	Sharp	Sharp	Sharp
		19	0.0359	56	Sharp	Sharp	Sharp
		14	0.0641	56	Sharp	Sharp	Sharp
		13	0.0719	62	Sharp	Sharp	0.0625''
Hard	4	26	0.0159		Sharp	0.0156''	0.0156''
		20	0.0139	76	0.0625''	0.1250''	a
		16	0.0508	75	0.0937''	0.1250''	a
		14	0.0641	75	0.1250''	0.1250''	a
		10	0.1019	75	a	a	a
Spring	8	24	0.0201	79	0.0312''	0.1250''	a
		20	0.0319	82	0.0937''	a	a
		18	0.0403	82	0.0937''	a	a
		16	0.0508	82	0.0937''	a	a
Extra Spring	10	26	0.0159		0.0156''	0.0937''	a
		24	0.0201	80	0.0312''	0.1250''	a
		22	0.0253	83	0.0625''	a	a
		20	0.0319	83	0.0937''	a	a

a None of the radii tested were suitable.

0.0625-in. bend could be made satisfactorily. In part B, it was desired to use extra hard temper high-brass sheet. Table 2 shows that the hardest material from which the part could be formed, using a 0.0312-in. radius, is hard temper and if this temper is used, it would be desirable to have the bend perpendicular to the direction of rolling of the metal.

CONCLUSIONS

Data on forming tests are summarized to show the minimum radii of 90° forming tools that produce acceptable bends in some thicknesses and tempers of some brass, phosphor bronze and nickel-silver sheet.

A numerical relationship between the thickness of the sheet and the radius of the tool that forms acceptable bends is not attempted in view of the effect of variation in grain size, temper and composition of the materials.

Experience in the application of the data presented has demonstrated the practicability of using them in designing formed parts and forming tools.

DISCUSSION

(J. L. Christie presiding)

E. V. CRANE, New York, N. Y.—I agree with the authors that there is very little literature on bending operations. As a matter of fact, one of the things we would very much like to have is a good formula for figuring with the resistance we meet in bending operations. The static form of beam formulas appears to give very low results. We sometimes take as a supposedly safe figure the ultimate strength of the stock across the section that is being stressed. But if the bend is a hit-home operation in a V-die such as the authors showed, the actual pressure may exceed the ultimate section strength, due to a coining load.

D. K. CRAMPTON, Waterbury, Conn.—There are three points that perhaps were not brought out in as great detail as they might have been in the paper.

The first point is the effect of lead in high brass. The authors did not give the exact analysis of the material used but simply stated the nominal analysis to which the material is brought. Probably in at least 90 per cent. of the cases where high brass is used, lead within the limits specified would be of little importance, but in a case where material was just on the verge of failure, that is, showing an incipient failure, it is quite possible that a lead content up toward 0.3 per cent., the limiting concentration here, would cause trouble, whereas a lower lead content would not cause trouble.

The second point is a caution in the use of the data as regards the total angle through which the material is bent. The authors used 90°, and if in a given instance material is to have a greater included angle left, obviously material a little bit harder or with a sharper punch could be used, whereas if the angle through which the material is bent is more than 90°, leaving an included angle of less than 90°, a material not quite as hard would have to be used.

The third point is with respect to grain size. I do not know whether the authors went into that or not, but there was some indication that in a good deal of bending grain size previous to the last reduction has an appreciable effect.

J. R. Townsend, New York, N. Y.—The authors are to be congratulated on the development of such a simple test which can be directly applied in engineering design and use of materials. The test is in a class with some of the useful and simple tests which many of us now employ, such as the dynamic ductility test that was developed for sheet zinc by Trewin and Finkeldey and the method of testing the corrosion properties of sheet metal by measuring the loss in tensile strength of the sheet metal after it has been exposed to corrosion, which was a suggestion made by Dr. Blough.

There is an interesting point in connection with this test. I have taken the data and plotted the thickness of the metal against the radius of bend that could be safely made without undue cracking, and the result is practically a straight-line curve relation. There is some variation with points off the curve but these points must be due to not selecting the correct end point. More samples at each point would give a truer value and I believe all average points so determined would lie on a straight-line curve.

In other words, a number of specimens should be taken at each particular radius, because there seems to be a spread in the material which may be due to variations in composition and in the anneal previous to the final reduction. We have tried a number of sheet metals by this method and find the application very simple and rapid. It is easier to apply than a hardness test.

W. R. Webster, Bridgeport, Conn.—Should not the title of the paper be "Bending Properties of Sheet Metal" rather than "Forming Properties," as ordinarily we associate the word "forming" with considerable distortion?

W. A. Straw, M. D. Helfrick and C. R. Fischrupp (written discussion).—The data presented were obtained for use in estimating the temper of the metal and radius of bend that would be satisfactory for miscellaneous telephone-apparatus parts which require severe bending. The study was not a scientific investigation of "formability" or an attempt to correlate forming characteristics with other properties. Further, the effects of variations in the concentration of impurities and in the grain size on the forming characteristics of the materials were not investigated. We agree with Mr. Crampton, however, that in case a nonleaded material showed an incipient failure, material of the same grain size and temper having 0.3 per cent. lead might crack if subjected to the same bending. Also, we agree that abnormal grain sizes might noticeably affect data on forming characteristics.

We agree with him also that caution must be exercised in the use of the data where the included angle at the bend will be greater or less than 90°. In addition to this caution, we wish to point out that in using the data one must also consider the possible effect of the type of bending tool used and of peculiarities in the design of the parts under consideration.

Referring to Mr. Townsend's comments, it is true that within certain limits the data indicate a straight-line relationship for a given alloy and temper. The fact that some points are out of line is not surprising in view of the number of factors that may affect the results. It is possible that if more specimens had been tested at each point, a truer value would have been obtained and the average point so determined would lie on a straight-line curve. However, when these tests were made, if there appeared to be a variation among the three specimens which were formed over each radius, further tests were made on the material. It is possible that obtaining a straight-line curve is a question of testing, at each radius, material which represents several different lots of metal. Curves showing the above relationship were not included in the paper because it was believed that sufficient thicknesses had not been investigated

in the various tempers and alloys to furnish conclusive evidence as to how the curves should be drawn.

We agree with Mr. Webster that the operations involved in this test are of a bending character. We preferred the word "forming" in order to indicate that the test is a "hit-home" punch-press operation and not a reverse bending test such as that made on the Amsler machine, or a 180° bend test in which the material is folded back on itself.

Die Pressing of Brass and Copper Alloys

By John R. Freeman, Jr.,* Waterbury, Conn.

The die pressing of brass may be described as a method of producing irregularly shaped parts of brass and other copper alloys by hot deformation in a die under pressure. Die pressing of brass was first developed as an improvement on sand castings in order to obtain irregularly shaped articles of brass with superior surfaces, a closer tolerance in dimensions, a denser structure, freedom from porosity and elimination of the relatively large amount of scrap invariably attached to sand castings. The freedom from sandy surfaces with consequent greater tool life in machining operations was also recognized as well as elimination of losses due to the uncovering of blowholes in machining operations. Die pressing also gave alloys of superior strength.

Die pressings today are made from extruded rod or shapes, according to design of the part to be made. The greater number of pressings are made from round rod, because of its relatively lower cost and ease of handling. The rod is first sheared or sawed into desired lengths, the diameter of rod used and length of "slug" or "rivet" depending upon ultimate weight and shape of the die-pressed part to be made and design of die. The dimensions of the slug are figured so as to give the minimum amount of scrap to be sheared from the pressing as it comes from the die.

Extruded shapes having I, T or X sections are often used when the finished part is to have a similar shape or heavy sections are joined by relatively light sections of considerable length. A rod bent in the shape of a U is also used on occasion, for similar reasons.

Proper shearing of the slugs is of considerable importance. The sheared ends of the slugs should be as flat and straight as possible. Improperly sheared ends having an angle to the axis of the bar or a rough, uneven surface are liable to give folds or laps in the finished pressing and proportionately high rejections. The property of shearing varies considerably with different alloys and should be considered in the selection of a material for a given part. Where satisfactory shearing is not possible, the slugs may be cut from the bar by power saws. Extruded

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* American Brass Co.

shapes are generally sawed to length. Shearing is obviously preferable because of greater speed and no waste of metal.

The die pressing of the slug to desired shape usually is carried out in either a drop, crank or screw press. The drop press is preferred because of its greater speed of operation and is almost always used for making small parts. Its use is primarily limited by the capacity of the hammer. The screw press (air controlled) is generally used for the forming of larger parts; also for some alloys and shapes the relatively slower flow of the metal in the dies and extrusion action of the press is preferable. Presses of 250 up to 800 tons capacity are now used.

The design of dies is of major importance. For most work two-piece, so-called "open" dies, are used; Figs. 1 to 4 show design of die used for making parts shown as *A* and *B* in Figs. 8 and 9.
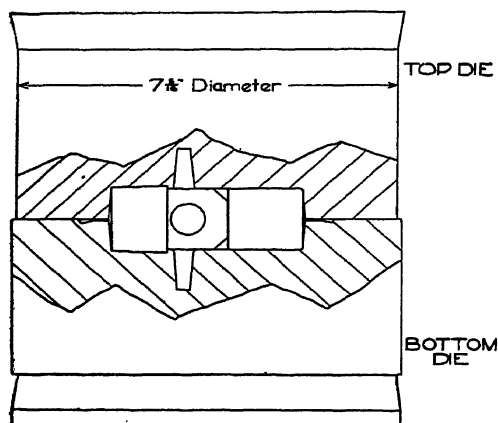
FIG. 1.—TWO-PIECE DIE FOR PRESSING BRASS VALVE BODY SHOWN IN FIG. 8.

Die design is based primarily on experience. When possible the upper die is designed to act as a ram to force the metal to flow into the cavities in the lower die that give the desired shape to the metal. This places the greater wear on the lower die; consequently the upper die has a longer life, which necessitates less frequent replacements of the latter and often permits use of a less expensive steel in the upper die. The draft in the upper and lower dies is generally adjusted so that after forming the part will pull free from the upper die and remain in the lower one, to permit quick and easy ejection by the knock-out pins in the bottom of the lower die. The draft will vary from 1° to 5° according to design. In addition to proper draft, a flash clearance of 0.023 to 0.080 in. must be allowed, according to design of part, as well as proper allowance for thermal shrinkage of the metal. usually about 0.012 in. Die-press pieces

under certain conditions. Parts to be made in two-piece dies necessarily must be free from undercuts.
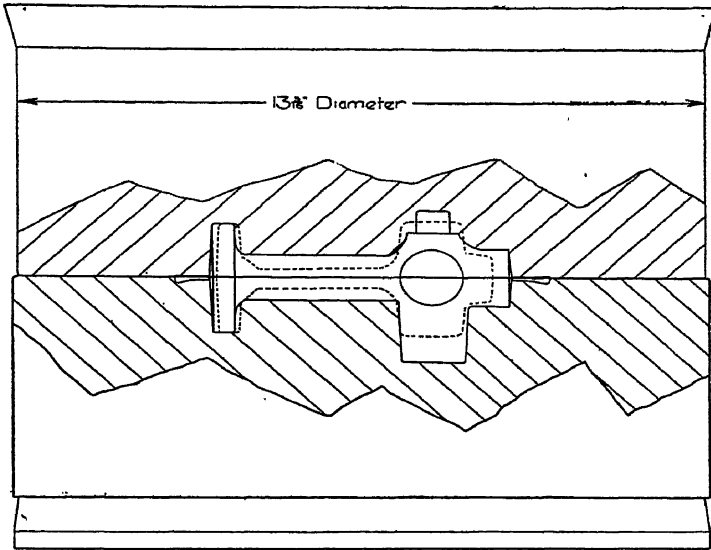
FIG. 2.—TWO-PIECE DIE FOR PRESSING BRASS VALVE BODY SHOWN IN FIG. 8, ILLUS-
TRATING USE OF EXTRUDED SHAPE INDICATED BY DOTTED LINES.

When the design calls for recessed or offset portions in such a position that they cannot be placed at the parting line of a two-piece die, a split
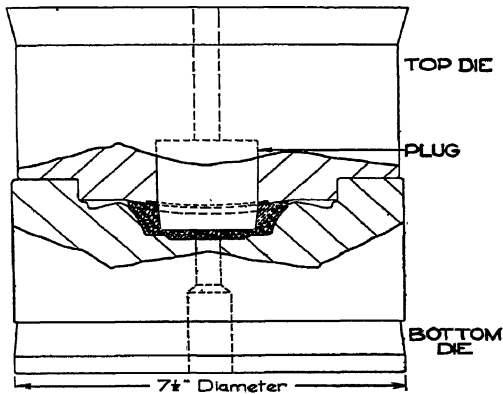
FIG. 3.—TWO-PIECE DIE WITH PLUG FOR FORM-
ING EVERDUR SPUD SHOWN IN FIG. 9.
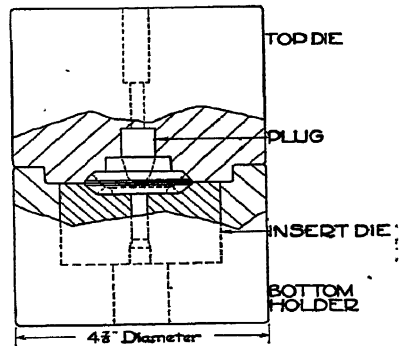
FIG. 4.—TWO-PIECE DIE WITH
PLUG AND INSERT DIE FOR FORMING
BRASS GEAR SHOWN IN FIG. 9.

die is used. The design of such dies is similar to two-piece dies except that the lower die is split vertically and fits into a tapered die bed of 25°

angle, so that when pressure comes against the bump the dies are held firmly together. After the press reverses, an automatic knock-out raises
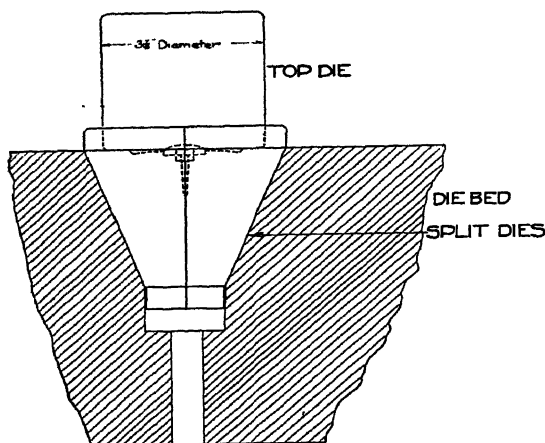
FIG. 5.—SPLIT DIE FOR FORMING PART HAVING UNDERCUT PORTION AS SHOWN IN FIG. 9.

the split dies against a stop which opens the dies and permits easy ejection of the parts. The split dies then drop back into original position.

FIG. 6.—THREE-PIECE DIE FOR FORMING RING SHOWN IN FIG. 9.

A die of this type is shown in Fig. 5; the part formed is marked C in Fig. 9.

A third type of die generally referred to as a three-piece die, or an "extrusion" die, is shown in Fig. 6. It is made up of three parts, the bottom die and the upper die block which consists of two parts, the container die and the punch. In operation the container die first closes into the recess in the lower die. The punch then is forced further down, forcing or "extruding" the metal slug into the cavity. A die pressing formed in this type of die is shown at D in Fig. 9.

The principal cost of die pressing is the initial cost of dies and their service life. The number of parts obtained from a set of dies depends on many factors. Parts requiring relatively long thin walls with sharp corners and considerable flow of

metal are especially severe, causing early checking of the die. Die life is also limited by the dimensional tolerances required, a close tolerance causing earlier discard of the die. In general, a tolerance of ± 0.010 in. is preferred, but a tolerance of ± 0.005 in. can readily be maintained. A die usually is designed so that when new the part will be slightly undersized and as the die wears the part will approach the maximum permissible dimensions. An average of about 30,000 parts may be expected from a die.

Die pressings are preferably made in one operation but in some cases the slug may be given a preliminary forming operation, then reheated and finished in a second pair of dies. For example, it is sometimes simpler and more economical to give a round slug a preliminary
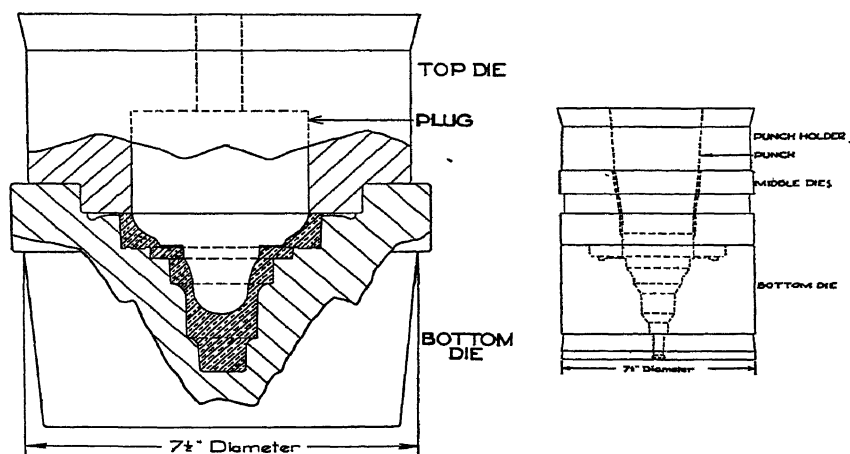
FIG. 7.—DIES USED FOR FORMING PART IN TWO OPERATIONS.
First operation is done in a three-piece die and final operation in a two-piece die. Part made is shown in Fig. 8.

forming operation than to use an extruded shape, or it may be simpler for parts requiring considerable depth of flow of metal into the die to carry out the operation in two steps. A die for the latter type of work is illustrated in Fig. 7 and part formed at C in Fig. 8. In this case the slug as sheared from extruded rod is given a preliminary forming in a container die. The flash is then removed, the part reheated and given its final form in the finishing die. The use of two operations for forming this pressing avoids folds in the metal and gives greater tool life.

The temperature of pressing will vary with the alloy and must be adjusted between too high a temperature, which will burn the metal, and too low a temperature, which will prevent the metal from filling the die. In the heating, scaling must be avoided. Scale gives a poor surface to the part, prevents filling of sharp corners and causes excessive wear on the dies.

After forming the flash is trimmed off and the center punched out if required. The sides, as in nuts, may be trued up if required, by a light broaching operation, which consists essentially in removing the draft angle. The die pressings are given a sulfuric acid and bichromate
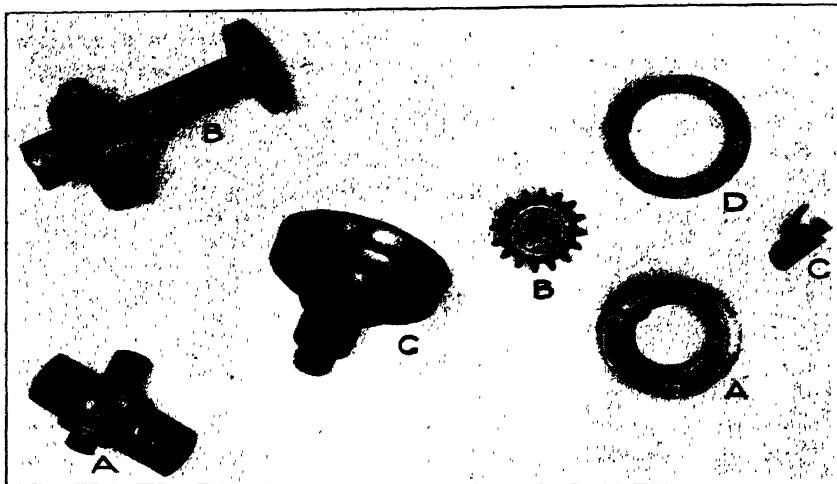
FIG. 8.   FIG. 9.

FIG. 8.—DIE PRESSINGS.
A. Brass valve body made in die shown in Fig. 1. B. Brass valve body made in die shown in Fig. 2. C. Part formed in two operations.
FIG. 9.—DIE PRESSINGS.
A. Everdur spud made in die shown in Fig. 3. B. Brass gear made in die shown in Fig. 4. C. Part made in die shown in Fig. 5. D. Ring made in die shown in Fig. 6.

pickle to remove superficial scale, then are washed, dried and packed for shipment.

Die pressings are made of most all of the copper-base alloys. The greater number are made of leaded high brass (about 60 per cent. copper, 2 per cent. lead, balance zinc) because of its good forging characteristics and excellent machining qualities. Large numbers are also made of the aluminum bronzes, manganese bronze, Tobin bronze, nickel silver and more recently of Everdur.

ACKNOWLEDGMENTS

The author wishes to acknowledge the cooperation and assistance of Mr. A. V. Pollard and Mr. L. Heady in the preparation of the manuscript.

DISCUSSION

(J. L. Christie presiding)

D. F. McFARLAND, State College, Pa.—I am much interested in this paper because it bears on some work that has been carried on in our laboratory by Prof. O. B. Malin

in conjunction with the plant that is near us, on the flow of the metal in the forging operation and the effect it has on certain inherent defects in the forging, the relation between that and the original extrusion of the rod from which the slug is made. We have found that the extruded rod has a very different grain structure when the first part is extruded as compared to the last part through the extrusion die, and that that difference carries along into the grain structure and the rate of flow into a complicated die in the forging operation, and that some of the defects which appear frequently in the forged material can be traced to the difference in rate of flow between the material of large grain size and that of small grain size coming from different parts of the rod. Usually the difficulty can be corrected by a redesign of the die.

S. Tour, New York, N. Y.—I would like to call attention to a rather new development that has been mentioned once or twice recently in the literature but has not become very well known in this country as yet; that is, the process which might be called the press-casting process. Referring to Fig. 1 in Mr. Freeman's paper, the valve body as a die pressing must be made as a solid piece of metal, then the body must be drilled or bored out for the final use of the valve. In the press-casting operation it is possible to cause the metal to flow around cores; this particular part would then be made with a core in it, and the machining operation would be eliminated. The difference between the press-casting method and the die-pressing method is that in general in die pressing the metal flow is in one direction, that is, it will flow up around the punch or it will flow out into the die, whereas in the press-casting method the metal can be made to travel around cores, into lugs, around corners, through thin sections into thick sections, changing directions as necessary, and make a completed casting with cored holes.

The press-casting process is in rather general use in Europe and it is expected that there will be considerable commercial application of it in this country within another year.

J. R. Freeman, Jr.—We would be much interested in seeing the more detailed discussion of the work that Professor McFarland mentioned, which should be of great help in some of the problems encountered in die pressing. We will also be interested in knowing more about the press-casting operation mentioned by Mr. Tour.

Plasticity of Copper-zinc Alloys at Elevated Temperatures

By Alan Morris,* Bridgeport, Conn.

The investigation of the hot-working properties of metals and alloys furnishes a problem which has been attacked in many ways. Tensile, impact and hardness tests on heated specimens have furnished interesting data, but in most cases either the tests are difficult to make or the results hard to translate into terms of practical value. Some investigators have used the drop hammer to advantage. It furnishes a rapid and simple method of comparing the plasticity of metals at elevated temperatures. The indications obtained by its use are of value only in so far as their significance is understood and they can be intelligently used to predict the behavior of a given metal under given hot-working conditions. The work reported here was undertaken not only to add something to the existing volume of such data but also to contribute to our understanding of the results.

Doerinckel and Trockels[1] used cylindrical specimens and determined the work required to reduce the specimen to one-half the original height. Ellis[2] studied the effect of constitution on the malleability of steel at high temperature. His method and that of Kent[3] were similar to the one used in the present work.

The tests described by Kent were made on samples of tin, zinc, aluminum, copper, lead, 70:30 and 60:40 brasses, with and without a small quantity of lead. He concluded that the test would "indicate whether a material can be forged at a given temperature without cracking." This interpretation must be used with caution. While it is probably true within limits, one must consider the severity of the forging operation. Again, it will not apply strictly to forms of hot working other than forging. For instance, an alloy running 61.0 per cent. copper, 3.25 per cent. lead, remainder zinc, will crack badly in the test, yet it is extruded commercially. When the possibility of hot-working a new alloy is being considered a study of its drop-hammer test should help

[1] F. Doerinckel and J. Trockels: Über die Stauchbarkeit von Messing Verschiedener Ziesammensetzung in Abhängigkeit von der Temperatur. Ztsch. f. Metallkunde (1920) 12, 340.

[2] O. W. Ellis: Investigation into the Effect of Constitution on the Malleability of Steel at High Temperatures. Carnegie Schol. Mem., Iron and Steel Inst. (1924), 13, 47.

[3] W. L. Kent: Behavior of Metals and Alloys During Hot Forging. Jnl. Inst. Metals (1928) 39, 209.

to answer such preliminary questions as: (1) Is it likely to develop high roll pressures? (2) Is it sufficiently plastic within the possible temperature range to be pierced on a Mannesmann machine? (3) What temperature is necessary to render it sufficiently soft for extrusion?

PREPARATION OF SAMPLES AND METHOD OF TEST

Preliminary tests were made on samples turned from castings and on some that had been forged. As the results practically checked, there seemed to be no reason to use cast samples. As a matter of expediency, therefore, the samples used were cut from forged rod. The metal was
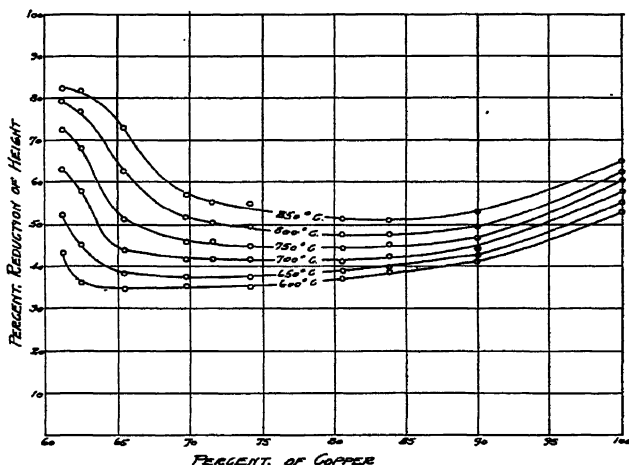
FIG. 1.—PLASTICITY OF COPPER-ZINC ALLOYS INDICATED BY DROP-HAMMER TEST ON HEATED SAMPLES.

cast in chill molds $1\frac{1}{8}$ in. inside diameter by 12 in. long. The cast billets were forged to $\frac{5}{8}$ in. and annealed for 1 hr. at 600° C. The test samples were machined from the forged rod thus produced.

Cylindrical slugs of metal $\frac{3}{4}$ in. long by $\frac{1}{2}$-in. dia. were heated to the desired temperatures in a small resistance furnace, which was placed close to the anvil of a drop hammer. The hammer weighed 50 lb. and fell through a distance of 4 ft., striking a blow of 200 ft-lb. When the samples had reached the desired temperature they were quickly transferred from the furnace to the anvil, and the hammer was dropped. The sample was placed on the anvil in an upright position, so that the blow was struck in an axial direction. The time interval between the removal of the sample from the furnace and the instant the blow was struck was less than one second, so that the cooling was insignificant. The length of the sample before and after the blow was struck was recorded and the difference between these two quantities, expressed as a

percentage of the original length, was calculated. All results plotted in this paper represent the mean of at least two determinations.

The so-called "normal" sample (one whose height is equal to its diameter) was not used, as it was felt that somewhat longer samples would give greater sensitivity, both as to cracking and reduction in height.

RESULTS OF TESTS

The results of tests on various brass mixtures are plotted in Fig. 1. The mixtures usually considered most difficult to hot-work show the least plasticity, or correspond to the lowest portion of the curves.
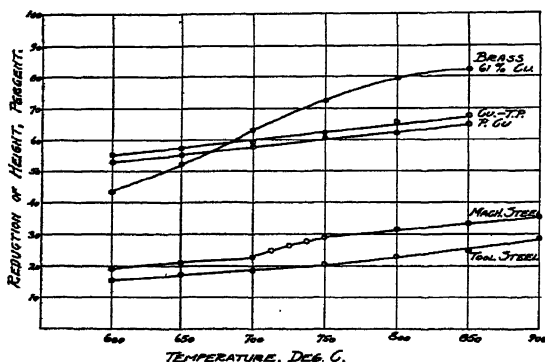
FIG. 2.—PLASTICITY OF VARIOUS MATERIALS, INDICATED BY DROP-HAMMER TEST ON HEATED SAMPLES.

Tests were made to determine the effect of overheating prior to testing. Samples containing 61.1, 62.5 and 65.4 per cent. of copper were brought up to 700° C. and subjected to the hammer blow. Similar samples were heated to 800° C. and held for 20 min., allowed to cool to 700° C. and struck; 800° C. is not sufficiently high to burn the brass, but does produce a coarse grain. The samples which had been so heated were slightly softer at 700° C., and showed a tendency to crack, which was lacking in the finer grained samples. As a rule, when the testing temperature was high enough to produce a coarse grain, the samples were likely to show tiny checks around the edge.

Fig. 2 shows phosphorized copper compared with tough-pitch copper. As a matter of interest, plots are also shown of the results of tests on high-carbon and low-carbon steel and on Muntz metal. The phosphor copper is slightly less plastic than the tough-pitch copper. Muntz metal at temperatures above 700° C. is considerably softer than either. The machine steel is somewhat softer than the tool steel and shows a sudden break at about 700° C., which checks fairly well with the results of Professor Ellis.[4] Analyses of materials tested are given in Table 1.

O. W. Ellis: *Op. cit.*

TABLE 1.—*Analyses of Materials Tested*

	Cu, Per Cent.	Pb, Per Cent.	Fe, Per Cent.	Zn, Per Cent.	P, Per Cent.	O, Per Cent.	C, Per Cent.
Fig. 1..................	61.10	0.35	0.04	Rem.			
	62.49	0.09	0.01	Rem.			
	65.41	0.05	0.008	Rem.			
	69.81	0.01	0.007	Rem.			
	71.62	0.024	0.01	Rem.			
	74.10	0.027	0.01	Rem.			
	80.64	0.021	0.016	Rem.			
	84.25	0.02	0.01	Rem.			
	90.00	0.009	0.012	Rem.			
Fig. 2							
Phos. copper.........					0.012		
Tough-pitch copper....						0.07	
Muntz metal..........	61.10	0.35	0.04	Rem.			
Mach. steel..........							0.27
Tool steel............							1.34

MATHEMATICAL ANALYSIS

An attempt has been made to calculate the resistance offered by the sample to the blow. The 2400 in-lb. of energy is translated into work of deformation, excepting that part of it which is absorbed by the anvil. As the anvil in this case weighed about 1300 lb., it is assumed that this loss was small. As the deformation progresses, the sample spreads out, offering a larger and larger cross-section to the action of the hammer. This area can be determined at any instant by the formula

$$A = \frac{V}{l},$$

where V is the volume of the test piece and l is the instantaneous length or height of the sample.

When a sample has been struck, the average area it has presented to the action of the hammer during deformation is

$$A = \frac{1}{l_1 - l_2} \int_{l_1}^{l_2} \frac{V}{l}\, dl$$

where A = average area,
l_1 = original length of sample,
l_2 = final length of sample,
V = volume of sample.
We can now set up the equation:

$$2400 = iA(l_1 - l_2)$$

where i is the average resistance of sample to deformation. This can be written

$$2400 = i \int_{l_1}^{l_2} \frac{V}{l}\, dl$$

$$= iV \int_{l_1}^{l_2} \frac{dl}{l}$$

$$= iV\,(\log_e l_1 - \log_e l_2)$$

$$= iV\left(\log_e \frac{l_1}{l_2}\right)$$

Solving for i,

$$i = \frac{2400}{V \log_e \dfrac{l_1}{l_2}}$$

With this equation it is possible to calculate a compressive strength to correspond to any percentage reduction in height as reported in the
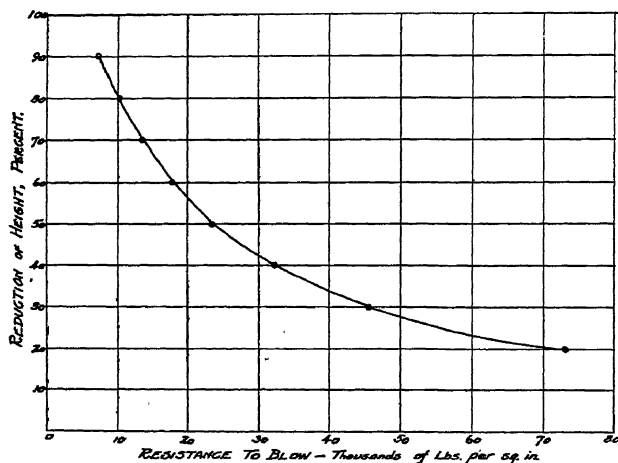
FIG. 3.—RELATION BETWEEN RESISTANCE TO BLOW AND REDUCTION OF HEIGHT.

tests. The relation is shown in Fig. 3. The results plotted, of course, hold only for a 200 ft-lb. blow on a sample of the size used.

Table 2 lists the results of Kent's tests on 72:28 per cent. brass and tough-pitch copper, reduced to terms of resistance to the blow, in comparison with results obtained in the present work. Kent used "normal" ½-in. samples and a 50 ft-lb. blow.

The results appear higher than one might expect. The extreme rapidity of the deformation under the hammer blow seems to be mainly responsible for this. To learn something of the magnitude of this factor,

samples of lead, tin, aluminum and zinc were tested under the drop
hammer at room temperature. Similar samples were then given a

TABLE 2.—*Comparison of Tests*

Temperature, Deg. C.	Tough-pitch Copper, Lb. per Sq. In.		72:28 Copper-zinc Alloy, Lb. per Sq. In.	
	Kent	Present Work	Kent	Present Work
600	20,600	20,500	32,000	38,000
650	19,500	19,100	33,500	35,000
700	19,300	18,000	32,000	30,500
750	18,500	16,900	29,900	27,000
800	16,900	15,200	25,400	23,500
850	15,400	14,300	21,100	20,500

TABLE 3.—*Results of Tests at Room Temperature*

Material	Reduction in Height by 200 ft-lb. Blow, Per Cent.	Calculated Resistance to Blow, Lb. per Sq. In.	Plastic Flow Point, Shown by Static Test, Lb. per Sq. In.
Lead......................	83.0	9,000	3,500 to 4,500
Tin.......................	63.0	16,000	4,000 to 7,000
Aluminum................	46.0	26,500	20,500 to 25,500
Zinc......................	20.5	71,000	29,000
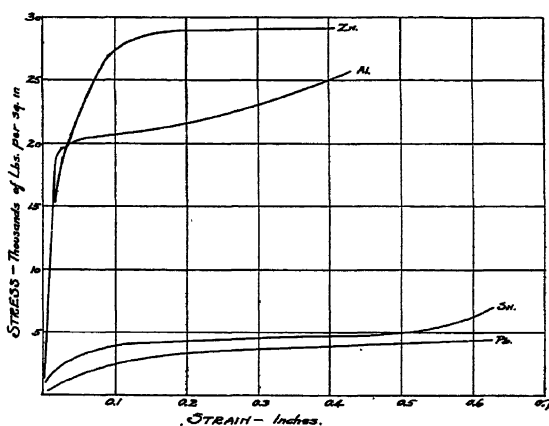
FIG. 4.—STATIC COMPRESSION TESTS ON LEAD, TIN, ALUMINUM AND ZINC AT ROOM
TEMPERATURE.

compression test in a standard testing machine (Fig. 4). Table 3 brings
all the results together. These show that, at room temperature: (1)
different metals react differently; (2) of the four metals tested, aluminum
shows (a) the smallest increase in resistance due to speed of deformation

and (b) the greatest tendency to strain-harden; (3) zinc has (a) the greatest increase in resistance due to speed of deformation and (b) the least tendency to strain-harden.

SUMMARY AND CONCLUSIONS

1. A series of drop-hammer tests at elevated temperatures has been made on brasses ranging upward from 62.0 per cent. copper. The alloys usually considered most difficult to hot-work show the least plasticity.

2. The drop-hammer test as a means of predetermining whether a metal or alloy will crack in hot working must be used with judgment, since the severity and nature of the hot-working process must be given due weight.

3. Alpha brasses that have been heated so as to develop a large grain appear to have a greater tendency to crack than samples of the same alloy that have not been so overheated.

4. A method of calculating the average resistance of the sample to the blow is offered, which may prove to be a means of correlating the work of various investigators, though they have used samples of different sizes and different weights of blow.

5. The calculated resistances of lead, tin, aluminum and zinc at room temperature are compared with the plastic flow points, as determined by ordinary test. The relation between these two quantities varies with the different metals. The calculated resistances of lead, tin and zinc are much higher than the plastic flow points, while in aluminum the difference is not so great. This difference is mainly accounted for, probably, by the greatly increased speed of deformation under the hammer, but to some extent may be due to strain-hardening.

ACKNOWLEDGMENTS

The author thanks the Bridgeport Brass Co. for permission to publish these data, and acknowledges gratefully the suggestions and counsel of Mr. W. R. Webster and Mr. W. R. Clark.

DISCUSSION

(J. L. Christie presiding)

E. V. CRANE, New York, N. Y. (written discussion).—In Table 3 and conclusion 5, Mr. Morris illustrates clearly considerable differences in plastic resistance at room temperature, due to differences in working velocities, for tin, lead and zinc, but shows no difference for aluminum. We appear to have here an excellent illustration of the desirability of recognizing the recrystallization temperature range of the particular metal as the boundary between *hot* and *cold* working. There seems to be reason to believe that working a metal above its recrystallization temperature at low speeds permits some intercrystalline movement which materially lowers its plastic resistance. (Possibly a comparison may be drawn here with intercrystalline fatigue failures of cold metals.) As the speed increases, the movement must become wholly trans-

crystalline and the resistance no longer changes with the speed. This should account for the differences in the static and dynamic tests of lead, tin and zinc, all of which are in or above their recrystallization range. Due to more or less spontaneous annealing, they should show little or no strain-hardening in Fig. 4, which seems to be the case.

Aluminum, however, is distinctly being cold-worked at room temperature, and should show about the same unit stress resistance for the same amount of strain-hardening, regardless of the difference in working speed. This seems to be approximately true, if the calculated 26,500 and recorded 25,500-lb. stresses represent the same amount of working applied to similar initial blanks.

In Figs. 1 and 2, Mr. Morris has a most interesting illustration of the decrease in rate of strain-hardening as the temperature increases. It is probably unnecessary to point out how well these figures show the greater plasticity, or lower rate of strain-hardening, in the forging range of beta brass as compared with the higher alpha brasses.

The narrow range in which all-beta brass exists, even at forging temperatures, and the proximity of the brittle gamma constituent, is nicely brought out by diagram and photomicrographs in the paper of Mehl and Marzke.[5]

J. J. KANTER, Chicago, Ill. (written discussion).—Mr. Morris' paper stimulates interest in the development of a simple and effective means of studying the hot-working properties of metals. The drop-hammer test undoubtedly is a good basis of comparison for the behavior of metal during dynamic and impact deformations. It is somewhat to be questioned that drop tests are reliable criteria of the rolling and extruding characteristics, particularly from a quantitative standpoint. The author proposes a formula for calculating the pressure or resistance developed during deformations by impact. Furthermore, he shows that static resistance to reduction in height, unfortunately, is not reliably reflected by the drop test. This seems to emphasize the need of more actual data at elevated temperatures on the resistance of metals to compression and extrusion. The experimental difficulties involved in such tests undoubtedly have retarded serious attack of the problem.

Mr. Morris, however, gives an interesting cue for calculating the comparative resistances found in various drop test investigations, and an analysis of the problem is ventured here from a somewhat different viewpoint. We are often reminded that a mathematical analysis is no better than the assumptions which it involves. An analysis of the impact resistance problem necessarily rests upon the type of stress-strain relation hip assumed to hold for impact. It seems reasonable that when a sample has been struck, appreciable plastic deformation does not take place until a resistance of yield point magnitude has been built up. High-frequency fatigue testing indicates with sufficient approximation that rapid application of stress does not materially alter the normal stress-strain relationship at intensities up to the elastic limit and possibly the yield point.

If this be true, the greatest part of energy absorption in impact must take place under resistances in excess of the sample's yield or flow point. The work absorbed in raising the resistance to the yield point is negligible compared to the part entering plastic deformation. It is not clear that Mr. Morris' analysis adequately provides for the resistance which accrues during plastic deformation through strain-hardening. Such resistance should be considered additive to the yield stress. Yielding without increase of resistance is found only to a limited extent in soft steel. Such a picture is not general enough for the present problem. Strain-hardening, as well as variation in yield point, is a vital consideration to the analysis.

The following formulas suggest the effects upon impact resistance which probably arise from differences in yield point. Fig. 5 illustrates the effect with values computed

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for the sample and blow used in Mr. Morris' tests. The relationship between yield point, reduction and resistance is represented by a series of curves corresponding to a chosen yield value from zero to 40,000 lb. per sq. in. The lower the yield point, the higher is the reduction required to produce a given value of final resistance. The curves represent consistently higher resistance values than obtained by Mr. Morris.

A singular observation is that Mr. Morris' curve (dotted in Fig. 5) intersects each yield point curve at an impact stress equivalent to the yield stress for which plotted. In other words, from the standpoint of the writer's analysis, the Morris curve represents the reduction resulting if the final resistance were equivalent to the yield point of the material. This obviously would be a very special case, probably never obtained
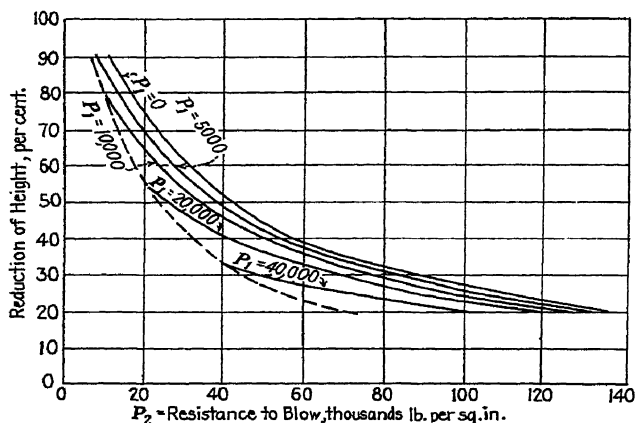
FIG. 5.—RELATION BETWEEN RESISTANCE TO BLOW AND REDUCTION OF HEIGHT. P_1 = yield point of flow stress, pounds per square inch. Dotted curve, plotted for $P_2 = P_1$, coincides with curve given in Fig. 3.

physically. The analytic derivation of this interpretation of Mr. Morris' formula is given below.

Granting that the relationship $A = V/l$, using the author's notation, is a sufficiently good approximation of the average cross-sectional area at any instant during deformation, it is clear that

$$dW = PAd(l_1 - l) = -PAdl = -\frac{PV}{l}dl \qquad [1]$$

where

W = work absorbed in deformation,
P = instantaneous unit resistance,
PA = total instantaneous resistance.

Since it has been argued above that the bulk of energy is absorbed under deformation above the yield point under strain-hardening conditions, resistance can be set up as a function of height reduction; such a function obviously differs with the metal considered. For the sake of simplicity, it is assumed here that the hardening is linearly proportional to reduction. This assumption probably gives resistance values somewhat lower than actual. Hence

$$P = P_1 + h(l_1 - l) \qquad [2]$$

and

$$P_2 = P_1 + h(l_1 - l_2) \tag{3}$$

where

P_1 = yield or flow point of sample,
P_2 = final resistance of sample,
l_1 = original length of sample,
l_2 = final length of sample,
h = constant depending upon the strain-hardening characteristics of sample.

We can now set up the equation:

$$W = -\int_{l_1}^{l_2} \frac{PV}{l} dl = +\int_{l_2}^{l_1} \left[\frac{P + hl_1}{l} - h \right] dl \tag{4}$$

$$= V\left[(P_1 + hl_1) \log_e \frac{l_1}{l_2} - h(l_1 - l_2) \right]. \tag{5}$$

$$= V\left[P_1 \log_e \frac{l_1}{l_2} + hl_1\left(\log_e \frac{l_1}{l_2} - 1\right) + hl_2 \right]. \tag{6}$$

From equations 3 and 6,

$$\frac{h}{l_2} = \frac{P_2 - P_1}{\left(\dfrac{l_1}{l_2}\right) - 1} = \frac{\dfrac{W}{V} - P_1 \log_e \dfrac{l_1}{l_2}}{\left(\dfrac{l_1}{l_2}\right)\left(\log_e \dfrac{l_1}{l_2} - 1\right) + 1} + P_1. \tag{7}$$

Solving for P_2,

$$P_2 = \frac{\left(\dfrac{l_1}{l_2} - 1\right)\left(\dfrac{W}{V} - P_1 \log_e \dfrac{l_1}{l_2}\right)}{\left(\dfrac{l_1}{l_2}\right)\left(\log_e \dfrac{l_1}{l_2} - 1\right) + 1} + P_1. \tag{8}$$

With this equation it is possible to calculate the impact compressive strength for any material where the linear strain-hardening assumption is a valid approximation. Similar formulas may be derived using various other functions to represent strain-hardening.

It is readily seen that if $P_2 = P_1$, the equation simplifies to

$$P_1 = \frac{W}{V \log_e \dfrac{l_1}{l_2}}. \tag{9}$$

which is the result obtained by Mr. Morris. Equation 8, the writer believes, affords a somewhat closer approximation to the actual physical picture than equation 9.

F. G. PARKER, Waterbury, Conn. (written discussion).—We have been using such a test as Mr. Morris describes and are pleased to see published such excellent data on this subject. Our results on different brasses show the same tendencies as found by the author, although we believe it is difficult to make a direct comparison in a quantitative way.

The drop hammer we use weighs 246 lb. and has an adjustable arrangement which permits it to be dropped from any predetermined height to deliver any blow between 200 and 600 ft-lb. The specimens are ⅝-in. dia. by 1 in. It is our practice to make five check tests on an alloy at three or more temperatures with three different blows at each temperature—200, 400 and 600 ft-lb.—to examine and note the surface condition and to determine the percentage of reduction in height.

In investigating the hot-working properties of an alloy, it is important to learn two things: (1) ease of deformation and (2) liability to crack. Each of these considerations is equally important whether we are attempting to determine hot-rolling, piercing, extruding or forging properties, and it is unfortunate that some form of surface rating has not been included in this paper. It is true that cracking depends on the severity of deformation as well as on temperature, and this is shown forcefully when testing a given alloy at a given temperature, but with different blows. It would be well to note that the tendency for surface cracks to develop in this test is much greater than in making a drop forging where the surface is constrained by a die. Often an alloy that shows slight cracks in this test will give a satisfactory surface with the same temperature in a drop forging.

It is also our practice to test specimens on their side instead of on end. Testing on end has as possible advantages: (1) offering a cross-section which is more nearly uniform during deformation; (2) allowing application of the formula given in this paper to calculate the unit resistance to deformation.

These are doubtful advantages, and in testing specimens on their side are more than offset by (1) ease of manipulation of slugs in removing them from the furnace with less loss of time and heat; (2) possibility of examining both sides and ends for surface cracks; (3) if specimens are cut from a drawn rod, it is not necessary to gage every slug before testing in order to calculate percentage reduction in height.

In the curve in Fig. 1 may be noted a peculiarity confirmed by Kent and by our work. In the lower copper brasses of the alpha + beta type, the rate of softening decreases with increasing temperature, while in brass of the single alpha phase the reverse is true. For instance, considering the 61 per cent. copper brass, in increasing the temperature 50° C. from 650° to 700° C., the percentage reduction of height increases about 10 per cent.; while in increasing the temperature 50°, from 800° to 850° C., it increases only about 3 per cent. In 90 per cent. copper brass, the corresponding figures are 2 and 4 per cent. respectively. In other words, as we approach the melting point in an alpha + beta brass the increase in softening becomes less for each degree of temperature rise, while in an alpha brass the reverse holds. This apparent anomaly is, we believe, due to the nature of the test and not to the intrinsic property of the alloy. When testing an alpha + beta brass which is very plastic at the temperatures where this discrepancy is noted, there is a large surface contact between the specimen and the dies during most of the period of the deformation because the height decreases 70 or more per cent., with proportionate spreading out. This increased area of contact means more heat loss to the dies, so that we are actually testing the alloy at a temperature lower than indicated. That this is the condition is shown by results we have obtained by testing brass of 60 per cent. copper at different temperatures with different blows. With the 200 or 400 ft-lb. blow, we did not find this discrepancy, but did with the 600 ft-lb. blow, because then the reduction of height had increased to such proportions (about 72 per cent.) as to show the effect of the heat loss. If this decrease in rate of softening had been a property of the alloy, we would have expected to find it at the corresponding temperatures with the lighter blows, but such was not the case.

In discussing these curves, the author says, "The mixtures usually considered most difficult to hot-work show the least plasticity or correspond to the lower portion of the curves." Here again we must note that plasticity tells only part of the story. The mixtures are considered difficult to hot-work, not so much because of the lack of plasticity but because of their great tendency to crack. From the curves, a mixture of 61 per cent. copper has a reduction of height of 52 per cent. at 650° C. Such an alloy can be easily hot-worked at that temperature. Now, also from the curves, a mixture of 70 per cent. copper would have the same plasticity as indicated by 52 per cent. reduction in height at about 800° C. These two alloys do not have equal hot-working

properties, the one at 650° C. and the other at 800° C.. even though this would be indicated by equal plasticity. The liability of the latter alloy to crack is so great that it is very difficult to hot-work it at any temperature.

Some results are given to show the effects of overheating, and the conclusion drawn that specimens of 61 to 65 per cent. copper overheated to produce a coarse grain are more liable to crack than others not so treated. We have not made any tests directly comparable to this, but we have noted that specimens of an alloy of 65 per cent. copper tested at 1100° F. had a surface which we rated "Fair" at the ends and "Excellent" on the sides; at 1300° F., "Poor" on both ends and sides, and at 1500° F., "Good" on ends and "Excellent" on the sides. Of course we realize that conditions of these two tests were not exactly the same. Our samples were heated to a certain temperature and tested at that temperature, while the tests referred to were made by heating to a higher temperature and then cooling and testing. However, even considering the difference in method, results appeared to be contradictory. From our tests, it appears that we pass through a brittle range in going from 1100° to 1500° F. Microexamination of our specimens that were tested at 1500° F. with no cracking shows the presence of beta phase, indicating that we passed into the alpha + beta field. It should also be mentioned that these results were obtained only with a 200 ft-lb. blow. With a 400 and 600 ft-lb. blow, these specimens cracked at all temperatures. Again we note that for successful hot working the correct combination of temperature and blow is necessary.

We have used these tests only as a means of comparing alloys when testing under exactly similar conditions. Employed in such a way, they have a distinct field of usefulness, but we do not believe that results can be compared to other work carried out under different conditions. For this purpose the author has developed an equation to determine the average unit resistance to deformation. We do not follow clearly in this derivation the establishing of the fundamental equation

$$A = \frac{1}{l_1 - l_2}\int_{l_1}^{l_2} \frac{v}{l_2} dl$$

In integrating the expression dl/l the limits are reversed. This would have no effect on numerical results, however, but would merely change the sign, one value being the resisting stress in the specimen and the other, equal and opposite, being the stress applied by the hammer. However, using the same terminology except that we will call the available energy E, and making the same assumptions, we arrive at the same equation. The area at any instant is $A = \frac{V}{l}$. The energy absorbed at any instant when the specimen is being deformed a differential distance is equal to the force, multiplied by the distance through which it moves, or $iA\,dl$, or $i\frac{V}{l}\,dl$.

The total energy $E = \int_{l_2}^{l_1} i\frac{V}{l}\,dl$

$$E = iV \int_{l_2}^{l_1}\frac{dl}{l}$$

$$E = iV \log_e \frac{l_1}{l_2}$$

$$i = \frac{E}{V \log_e \frac{l_1}{l_2}}$$

In the application of this formula we assume:

1. That the total available energy is absorbed in deformation of the specimen;

2. That during deformation the cross-section is uniform and that stress intensity is equal and uniform at any cross-section area;

3. That temperature remains constant during the deformation or else that it changes at a constant rate not affected by the volume of the specimen or its shape; *i. e.*, the ratio of its length to diameter;

4. That the effect of the speed of the blow on unit resistance to deformation does not vary with the speed;

5. That the effect of the blow on unit resistance to deformation does not vary with the energy of the blow.

These assumptions do not hold and, for that reason, the formula should not be applied. Part of the available energy is absorbed in the friction of the guides, in elastic deformation of the dies and in vibration. The amount of energy lost in this way would be different on different drop hammers, and probably different on the same hammer with drops of different heights. During deformation the cross-section is not uniform, but specimens bulge at the center. The temperature change in a specimen depends on its volume and shape. Large volumes lose heat more slowly than small. Specimens of equal volume but with large diameter in proportion to height lose heat to the dies very quickly because of the large surface contact. The effect of the speed and energy of the blow varies with the speed of the blow. The author has shown, in his tests on lead, tin, aluminum and zinc, the increased resistance to deformation in a drop test over a static test. We find this same difference in resistance to deformation between blows of different speeds. Table 4 gives some results of tests on brass.

TABLE 4.—*Tests on Brass Containing 61.07 Per Cent. Copper, 1.65 Per Cent. Lead, 0.05 Per Cent. Iron*[a]

Test No.	Diameter, In.	Height, In.	Volume, Cu. In.	l/D	Reduction in Height, Per Cent.	Calculated i, Lb. per Sq. In.	Blow, Ft-lb.	Free Fall, In.	Velocity, Ft. per Sec.	Surface	Increase in Circumference, Per Cent.
1	0.792	0.626	0.308	0.79	63.7	15,400	400			G	65.8
2	0.724	0.752	0.309	1.04	69.3	13,150	400			F	80.5
3	0.670	0.876	0.309	1.31	70.0	12,900	400			F	82.5
4	0.626	1.002	0.308	1.60	71.8	12,300	400			P	88.2
5	0.590	1.126	0.308	1.91	74.4	11,450	400			P	97.5
6	0.501	0.801	0.158	1.60	82.2	17,600	400			P	137.0
7	0.626	1.002	0.308	1.60	73.6	11,700	400			P	94.5
8	0.780	1.250	0.597	1.60	54.4	10,250	400			E	48.0
9	0.940	1.501	1.041	1.60	41.2	8,670	400			E	30.5
10	0.625	1.004	0.308	1.61	59.1	8,600	197	9.625	7.18	G	56.3
11	0.625	1.004	0.308	1.61	74.9	11,300	400	19.5	10.21	P	99.5
12	0.625	1.005	0.308	1.61	81.5	13,750	595	29.0	12.46	P	132.4

[a] All tests were made at 1400° F. All specimens were cut from the same rod. Each result is the average of five check tests. Specimens were tested on end. Surface readings are: E, Excellent; G, Good; F, Fair; P, Poor. E and G are considered satisfactory surfaces for a forging; F is doubtful and P is unsatisfactory.

The first five tests are specimens of equal volume but varying ratio of *l/D*. According to Mr. Morris' formula, they should all have equal percentage reduction of height and equal resistance to deformation. A decided increase in the reduction of height and

decrease in resistance to deformation, with increasing l/D due to different temperatures are noted, however, because of the different areas in contact with the dies.

Tests 6, 7, 8 and 9 are constant ratio of l/D but varying volume. Of course, as volume increased, the percentage reduction decreased, but calculated resistance to deformation, which should be the same, decreased with increasing volume. This was due to slower cooling of large volumes and a different rate of cooling because of the varying ratio of the surface contact area to the volume.

Tests 10, 11 and 12 are on identical specimens but with different energies of blow delivered at different speeds. The percentage reduction in height, of course, increases with increasing energy of blow, but calculated resistance, which again should be constant, increases with the speed of the blow.

In all these tests carried out on the same alloy at the same temperature, we should have equal values for resistance to deformation, while actually this calculated value varies from 8600 to 17,600 pounds per square inch.

Included in Table 4 is a column giving percentage increase in circumference. In examining surfaces, marked differences were found for slight variation in reduction of height. These edge cracks are probably due to tension stresses set up by increasing the circumference. Surface condition agreed very well with the figure for percentage increase in circumference.

Due to these discrepancies, obtained when using this formula, we do not believe that it can be employed for the purpose for which it was derived; i. e., the correlating of results of different investigators carried on under different conditions.

A. MORRIS (written discussion).—Mr. Crané's discussion suggests some interesting fields for speculation and further work. At present, the small amount of experimental evidence available makes generalization difficult.

Mr. Kanter questions the reliability of drop-hammer tests as criteria of rolling and extruding characteristics, particularly from a quantitative standpoint. Other variables, such as length and diameter of billet, size of extruded products, etc., make a definite quantitative application of these results to extrusion very complex. It is to be noticed that the author has made no attempt to translate these results into such quantitative terms. Our experience has demonstrated, however, that certain predictions of this kind may be made. For instance, we wish to extrude a metal M. We know that we can extrude another metal Q at temperature T. We make a drop-hammer test of metals M and Q and find that in order to obtain the same reduction in height as we find in metal Q at temperature T, we must heat metal M to temperature T'. T' is, therefore, the temperature at which we first try to extrude the metal M, with fair assurance that we shall be able at least to force the metal through the die. Much the same kind of reasoning can be applied to hot rolling. The tendency to crack in extrusion and rolling, however, must be ascertained largely through experience.

Mr. Kanter says, "We are often reminded that a mathematical analysis is no better than the assumptions which it involves. An analysis of the impact resistance problem necessarily rests upon the type of stress-strain relationship assumed to hold for impact." The author's formula is not based upon any assumed characteristics of the stress-strain relation of the material. It is in essence an expression of the average pressure which the sample must have exerted on the moving hammer in order to bring it to rest within the distance $(l_1 - l_2)$. A given material at a given temperature will have some sort of definite compressional stress-strain relation, at high rates of deformation. It may be of the type represented by the curve for lead in Fig. 4, or it may be more nearly like that for aluminum. But whatever its form, the pressure of the hammer against the sample at any instant is theoretically equal to the ordinate of the corresponding point on the curve. The value calculated by means of the author's formula, then, should be an approximation of the *average* ordinate of the stress-strain

curve between the limits of zero strain and $(l_1 - l_2)$. Furthermore, it represents this average value of pressure between hammer and sample, no matter what the strain-hardening characteristics of the material may be, or what its yield point. It is not at all an approximation of the yield point, as Mr. Kanter seems to believe.

The value for which Mr. Kanter has solved is the ordinate of the stress-strain curve at the point where strain equals $(l_1 - l_2)$. His method assumes the existence of a definite yield point of some magnitude corresponding to a relatively small strain, which is not a safe assumption. It would not be true, for instance, of lead or tin at room temperature.

The author finds it difficult to follow all of the steps in Mr. Kanter's derivation. For instance, in his equation 7 he has arrived at

$$\frac{h}{l_2} = \frac{P_2 - P_1}{\dfrac{l_1}{l_2} - l}$$

whereas the correct result seems to be

$$\frac{h}{l_2} = \frac{P_2 - P_1}{l_2(l_1 - l_2)}$$

This error is reflected in his final equation 8.

Even though we were to grant Mr. Kanter's assumption sound, and the method logical, if we knew enough about the hot-working characteristics of the metal to assign a value to P_1 in Mr. Kanter's formula, we would have no need of the drop-hammer test.

Mr. Parker's discussion indicates that he has probably done a greater volume of this type of work than has the author. By using varying blows and noting surface condition he has been able to learn something of the relative tendency of a material to crack in hot-working, which is a most valuable contribution.

Mr. Parker questions the validity of some of the assumptions made. He lists the assumptions, questions them, and offers the experimental evidence on which he bases his deductions. Unfortunately Mr. Parker has used a heavy blow on a very soft material. Almost all of his results approach or exceed 70.0 per cent. reduction of height. For reasons which will appear later, the results are misleading.

The author's first step in preparing an answer to this discussion was to repeat Mr. Parker's tests 1 to 9 inclusive, using a 50 ft-lb. blow instead of the 400 ft-lb. blow

TABLE 5.—*Results from Author's Repetition of F. G. Parker's Tests*

Analysis of Sample: Cu, 60.38 per cent.; Sn, 0.24; Pb, 1.87; Fe, 0.05; Zn, Rem. Blow, 50 ft-lb. Temperature, 1400° F.

Test No.	Reduction in Height, Per Cent.	Calculated i, Lb. per Sq. In.
1	21.5	8060
2	23.2	7360
3	24.1	7060
4	24.8	6850
5	26.0	6520
6	40.6	7300
7	25.8	6560
8	15.6	5950
9	9.5	5770

with the results shown in Table 5. These results are much more uniform than are Mr. Parker's. Despite the wide range of sample sizes and shapes, the average deviation of the individual results from the mean is only 8.0 per cent. However, the results vary in the same direction as do Mr. Parker's. He attributes this variation to loss of heat to the dies. Since the time factor is so small, this explanation does not seem a possible one. The author therefore repeated these nine tests with some intermediate points at room temperature. The results are shown in Table 6. The results still vary as in the hot tests. It is therefore quite evident that the variation is not due to loss of heat to the dies.

<div align="center">

TABLE 6.—*Results of Tests at Room Temperature*[a]
Blow, 200 ft-lb.:

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Test No.	Diameter, In.	Sample Length, In.	Reduction, Per Cent.	Calculated i, Lb. per Sq. In.	$l_1 - l_2$, In.	Observed Rebound, In.
1	0.792	0.6265	11.9	61,500	0.075	2.0
2	0.724	0.752	12.4	58,350	0.093	1.7
3	0.670	0.876	13.0	56,000	0.113	1.3
4	0.626	1.001	13.6	53,500	0.136	1.1
5	0.590	1.125	13.6	53,550	0.152	0.75
5a	0.437	0.700	28.1	69,400	0.197	0.8
6	0.501	0.801	21.5	62,800	0.172	0.7
6a	0.562	0.900	17.0	57,700	0.153	0.9
7	0.626	1.0025	13.6	53,100	0.136	1.1
7a	0.687	1.100	10.7	52,200	0.118	1.0
8	0.780	1.250	7.2	54,200	0.090	1.8
9	0.940	1.501	3.8	60,200	0.057	2.2

<div align="center">

[a] Material same as for tests of Table 5.

</div>

These tests also give us an opportunity to learn something of the energy loss by elastic deformation of the dies, etc. It seems reasonable to assume that the rebound of the hammer is very nearly a measure of the elastic loss. In the tests made at high temperature, there is no visible rebound. In these tests at room temperature, the rebound is seen to increase as $l_1 - l_2$ decreases. The energy lost through shock which expends itself in vibration of the floor probably varies in a similar way. In tests 5a to 9 inclusive (Table 6), the loss of energy due to elastic deformation of the system and to shock absorbed by the floor does not make itself felt until $l_1 - l_2$ is less than 0.118 in. As $l_1 - l_2$ drops below this value, the calculated i rises sharply.

It seems probable that these sources of energy loss again become large enough to introduce serious error when the conditions are such as to produce a very large reduction in height, as in Mr. Parker's tests. Here it is conceivable that most of the energy must be absorbed in the last small portion of the working stroke of the hammer.

Let us now consider the assumptions to which Mr. Parker takes exception:

1. "That the total available energy is absorbed in deformation of the specimen."

The energy absorbed in friction of the guides is negligible in any properly constructed hammer. It has been demonstrated that the losses by elastic deformation of the dies and by vibration are unimportant except in extreme cases not met with in ordinary tests at high temperature.

2. "That during deformation the cross-section is uniform and that stress intensity is equal and uniform at any cross-section area."

The formula is based upon an average area which is a mean between the original and final cross-section of the sample. The error introduced by the bulging of the sides is less than the probable experimental error.

3. "That temperature remains constant during the deformation or else that it changes at a constant rate not affected by the volume of the specimen or its shape; *i. e.*, the ratio of its length to diameter."

The author has demonstrated that temperature change in the specimen is not a factor.

4. "That the effect of the speed of the blow on unit resistance to deformation does not vary with the speed."

Tests which the author has made using a 100 ft-lb. blow produced by a 25-lb. and a 50-lb. hammer falling through 4 and 2 ft. respectively indicate that within the probable range of design of experimental hammers, the speed of the blow makes little or no difference. It must be remembered that the rate at which deformation takes place in any test varies from a maximum down to zero as the hammer decelerates.

5. "That the effect of the blow on unit resistance to deformation does not vary with the energy of the blow."

If the material under test is one which exhibits strain-hardening characteristics, Mr. Parker's objection to this assumption is well founded. The author has tested many materials with 100 and 200 ft-lb. blows of equal speed, and has found that the greater deformation produced by the heavier blow is accompanied by a slightly higher calculated resistance. This difference, however, is not large and when present has decreased with increasing temperature. In most cases it was negligible above 750° C.

The author feels that the drop-hammer test results are most dependable when the conditions are such as to produce reductions in height which are: (1) not so small that energy losses due to elastic deformation of dies and vibration become too large and (2) not so large that energy losses due to vibration and to surface friction between the sample and the dies become excessive. This latter source of loss has not heretofore been mentioned, but may be important.

Directional Properties in Cold-rolled and Annealed Copper*

By Arthur Phillips† and E. S. Bunn,‡ New Haven, Conn.

During the past few years considerable interest has been shown in the study of fiber, and its effect, in wrought metals. Fiber has recently been defined as a "condition of parallelism of important lines or details in the structure."[1] Briefly stated, two distinct types of fiber are commonly encountered. One results from the alignment in the direction of working of constituents, more or less segregated, such as slag, oxides, carbides and dendritic formations. The second, and least understood, type is produced by working the metal below the recrystallization temperature in such a way as to develop a parallelism of the grains. This condition is readily recognized by the pronounced elongation of the grains in the direction of working. Under certain deformational treatments the grain fragments produced by cold working tend to orient in certain definite directions with respect to the axis of extension. Furthermore, even in metals that have been annealed after cold working preferred orientations may be present.

It is perhaps logical to assume that such marked parallelism of structural elements would be manifested by directional properties in the metal. As a matter of fact, tests on many kinds of materials have shown differences in varying degrees. In recognition of this condition, proper design, for many purposes, places the fiber axis in such a way as to present the direction of maximum strength to the greatest applied stress.

Earlier Investigations

Howe[2] has written at considerable length regarding the causes and practical significance of fiber in steel and wrought iron. His studies showed that wrought iron and the puddled steel sheets (materials of plastic origin) were weaker transversely than longitudinally. The transverse deficit ranged from 5 to 29 per cent. The longitudinal tests

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* From a part of a report presented by E. S. Bunn to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Master of Science.

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[1] Definition proposed by Committee E-4 on Metallography, Amer. Soc. Test. Mat., June, 1930.

[2] H. M. Howe: Metallography of Cast Iron and Steel. New York, 1916. McGraw-Hill Book Co.

also yielded the better elongation values. In the steels of molten origin the distinction was not so apparent. In general, however, the longitudinal tests were superior in tensile and elongation properties. It should be noted in this connection that the data compiled by Howe represented tests obtained from many sources on commercial materials capable of forming, independently or collectively, several types of fiber.

In a series of tests carried on at the Watertown Arsenal[3] it was learned that test specimens cut longitudinally from shrapnel cases yielded markedly superior properties as compared with pieces cut tangentially; in other words, the best properties were to be found in the direction of rolling. As far as the authors are aware, Price and Davidson[4] were the first to publish tests on the directional properties of a nonferrous material. Further reference to their work on rolled brass will be made in a later section of this paper.

Mathewson, Trewin and Finkeldey[5] have determined the order of differences in tensile properties of pieces cut with and across the grain of soft-rolled strip zinc. Their observations indicated that the transverse pieces are superior from the standpoint of strength, but are inferior to the longitudinal strip in respect to ductility values. They believed that the differences in properties may be due to the fiber effect of iron and lead, together with the influence of preferred orientations assumed by the recrystallized grains.

Frequently in cupping, drawing or spinning of sheet material the presence of fiber is shown by the formation of "ears" or "scallops." The ears are usually located symmetrically with respect to the direction of rolling of the sheet or strip. Many instances of this nature have been encountered in the drawing of copper, brass, aluminum, nickel silver and iron. A specific example of ears on copper cups has recently been studied by X-ray methods.[6] It was shown that the copper that showed ears on drawing had a marked preferred orientation, whereas the copper of the same composition which did not ear under identical cupping conditions had a random orientation. It was concluded that an unusually heavy reduction prior to the last anneal was a contributing cause of the trouble, although it was considered probable that some other condition, not then determined, further complicated the solution of the problem.

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[3] Test of Metals, 1914.

[4] W. B. Price and P. Davidson: Physical Tests on Common High Brass Taken Parallel and at Right Angles to the Direction of Rolling. *Trans.* Amer. Inst. Metals (1916) **10**, 133.

[5] C. H. Mathewson, C. S. Trewin and W. H. Finkeldey: Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod. *Trans.* A. I. M. E. (1920) **64**, 305.

[6] A. Phillips and G. Edmunds: An X-ray Study of Copper Which Showed Directional Properties on Cupping. *Proc.* Amer. Soc. Test. Mat. (1929) **29**, Pt. II, 438.

As a result of an admittedly incomplete study of this subject, the writers believe that the pronounced directional properties found in the drawing of metals are often produced by the more or less supplementary effects of rolling and annealing treatments which are distinctly at variance with standard mill schedules. They are aware, of course, of the necessity for proper design and adjustment of the drawing tools and do not wish to imply that defects of the nature described are never due to tool trouble. There is reason for believing that extremely heavy reductions are to be avoided if uniform mechanical properties are desired. It is significant, moreover, that the chief offenders in this respect are the most ductile metals and alloys, such as silver, copper, aluminum and the high-copper brasses. In other words, they are the metals that are capable of undergoing large reductions in cross-section with few or, in some cases, no intermediate anneals. This possibility undoubtedly continually tempts the mill operator to utilize to a fuller extent the deformational capacity of the metal.

In spite of the considerable progress which has been made during the past 10 years on the subject of preferred orientations in rolled and annealed metals, due largely to the development of the X-ray spectrometer, there are surprisingly few data based on a comparison of strips cut in various directions as referred to the axis of extension. Furthermore, it is unfortunate that many of the X-ray studies have been confined to metal foils or, in most cases, to metal which has been plastically deformed to a greater degree than is commonly attained in mill practice.

In 1916, Price and Davidson[7] published the results of a comprehensive series of tests on the directional properties of cold-rolled brass. Their sheets of common high brass were tested longitudinally and transversely after reductions up to and including 86.7 per cent. The results of their investigation may be briefly summarized as follows: from the standpoint of tensile strength, the transverse and longitudinal test specimens were practically the same up to reductions of about 50 per cent.; beyond this reduction, the transverse tests were superior. Thus, at 66.7 per cent. reduction the transverse strength exceeded the longitudinal strength by about 3000 lb.; at 86.7 per cent. by some 9000 lb. per square inch. In other words, after the 86.7 per cent. reduction the transverse strength was approximately 9 per cent. greater than the longitudinal. With respect to the percentage of elongation, they reported that "up to 35 per cent. reduction by rolling, the elongations for both kinds of strip are practically identical, but from there on the transverse specimens showed marked superiority." The percentage reduction of area determinations on the strips cut with the grain were higher than the corresponding tests on specimens cut across the grain, up to reductions of 70 per cent., beyond which the writers considered the results to be untrustworthy. This

7 W. B. Price and P. Davidson: *Op. cit,* 142.

rather anomalous situation—the inconsistency between elongation and reduction of area results—is probably due to the difficulty of securing reliable test data on the thin strips of hard-rolled brass.

MATERIALS TESTED

As a preliminary step in the systematic study of the causes underlying the formation of ears and tips on drawn metals, it seems most advisable to obtain more abundant and more precise information regarding the directional properties of metals so treated as to cover a wide range of cold reductions and annealing temperatures.   In order to restrict the present investigation to channels furnishing data of practical significance, it was decided to avoid reductions and annealing treatments which are quite foreign to the conventional mill practices.

With this purpose in mind, copper was chosen for two reasons, in addition to its importance in industry; (1) because it is a metal that is prone to develop ears on drawing and (2) because it can be studied readily with or without a fiber constituent, depending on whether or not it has been deoxidized.   The authors wished to take advantage of this opportunity to consider the importance of cuprous oxide as a fiber element influencing the mechanical properties of rolled copper sheet.

The two kinds of copper chosen were (1) tough-pitch copper containing 0.0295 per cent. silver and (2) electrolytic copper deoxidized with phosphorus and containing 0.0089 per cent. residual phosphorus.   The authors are aware that it is not permissible to compare the properties of silver-bearing copper with electrolytic copper, or electrolytic copper treated with phosphorus.   The purpose was merely to compare the directional properties of copper containing its impurities in solid solution and to make the same observations on a second type of copper containing cuprous oxides as a mechanical mixture capable of being extended into a visible, though discontinuous, fiber.   The deoxidized copper, in spite of the 0.0089 per cent. residual phosphorus, contained 0.005 per cent.

TABLE 1.—*Analyses of Copper Tested*

	Deoxidized Copper,	Tough-pitch Lake Copper,
Copper, per cent...................	99.981	99.904
Silver, per cent...................	0.0028	0.0295 (9.45 oz. per ton)
Gold, oz. per ton...................	0.01	0.01
Arsenic, per cent...................	0.0017	0.002
Antimony, per cent.................	0.0019	0.0016
Lead, per cent....................	0.0011	0.0012
Phosphorus, per cent...............	0.0089	none
Oxygen, per cent..................	0.005	0.051
Iron, per cent....................	0.002	0.002

oxygen. According to Skowronski,[3] 0.025 per cent. phosphorus is now commonly specified for copper billets in order to insure complete deoxidation. The copper oxide content of the copper studied, too small in amount to be detected by microscopic means, may be considered as negligible in the present connection. Complete analyses of the two kinds of copper are given in Table 1.

TESTS ON COLD-ROLLED COPPER

The first series of experiments was confined to the study of the tensile properties of copper cold-rolled 10.5, 25.5, 36.4, 50.0, 60.5, 75.1 and 89.8 per cent. In order to avoid the variations in testing data, particularly in elongation values, associated with the testing of thin sheet material, the mill treatment was planned to end with material of the same thickness (nominally 0.100 in.) irrespective of the reduction. A brief outline of the rolling schedule is given in Table 2.

TABLE 2.—*Rolling Schedule, Deoxidized and Tough-pitch Lake Copper*

Final Reduction	10.5 Per Cent.	25.5 Per Cent.	36.4 Per Cent.	50.0 Per Cent.	60.5 Per Cent.	75.1 Per Cent.	89.8 Per Cent.
Hot Roll to 1.250	Hot Roll to 1.250	Hot Roll to 1.250	Hot Roll to 1.250	Hot Roll to 1.250	Hot Roll to 1.250	Hot Roll to 1.250	Hot Roll to 1.250
Overhaul 1.000	Overhaul 1.0000	Overhaul 1.000	Overhaul 1.000	Overhaul 1.000	Overhaul 1.000	Overhaul 1.000	Overhaul 1.000
Anneal 0.410	Anneal 0.410	Anneal 0.410	Anneal 0.410	Anneal 0.410	Anneal 0.410	Anneal 0.410	Anneal[a] 0.102
Anneal 0.258	Anneal 0.258	Anneal 0.258	Anneal 0.258	Anneal 0.258	Anneal 0.258	Anneal[a] 0.102	
Anneal 0.102	Anneal 0.114	Anneal 0.128	Anneal 0.162	Anneal 0.204	Anneal[a] 0.102		
Anneal[a]	Anneal[a] 0.102	Anneal[a] 0.102	Anneal[a] 0.102	Anneal[a] 0.102			

[a] Final anneals 500° C. Intermediate anneals 500–550° C.

Tensile test specimens were then cut from the sheets in three directions: (1) in the direction of rolling, i. e., with the grain; (2) at right angles to the rolling direction, i. e., across the grain; and (3) at 45° to the direction of rolling. Each test piece was then tested for strength, percentage of elongation in 2 in. and Rockwell hardness. Although it is freely conceded that the contraction of area is a highly desirable determination, probably more significant than the elongation value, no measurements of this kind were attempted because of the difficulty, if not impossibility, of securing reliable measurements on strip material.

The test data are summarized in Table 3; characteristic curves based on the same determinations are shown in Figs. 1 and 2. One of the

[3] S. Skowronski: Discussion of Some Comparative Properties of Tough-pitch and Phosphorized Copper. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 250.

TABLE 3.—*Tensile and Hardness Values of Cold-rolled Copper*[a]

Reduction of Area by Cold Rolling, Per Cent.	Test Specimens Cut Parallel to Direction of Rolling		Test Specimens Cut at Right Angles to Direction of Rolling		Test Specimens Cut 45° to Direction of Rolling		Rockwell Hardness, ⅛-in. Ball, 100-kg. Load, B Scale
	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	
TOUGH-PITCH LAKE							
10.5	35,600	36.3	34,850	37.50	35,370	28	81
25.5	41,350	16.2	42,600	10.5	41,350	10	90
36.4	47,150	7.8	48,600	6.5	47,600	7	94
50.0	51,300	6.2	53,700	4.8	50,100	6.2	95.5
60.5	54,600	5.5	57,500	4.4	54,300	6.7	97.5
75.1	59,000	6.	62,000	4.2	58,750	4.5	99
89.8	62,750	5.	64,600	4.	60,450	4.5	99.5
DEOXIDIZED ELECTROLYTIC							
10.5	37,400	35.	36,400	37.0	36,700	31.	86.5
25.5	41,100	17.	42,200	12.	41,100	12.	90.
36.4	49,950	7.5	51,000	8.2	49,925	8.7	96.5
50.0	53,350	6.	55,350	5.7	53,400	5.2	97.
60.5	58,200	5.5	61,100	5.2	57,900	6.	99.
75.1	62,300	5.5	64,600	4.2	61,000	4.	100.
89.8	64,400	5.7	67,350	4.	63,000	5.	101.

[a] Values are average of three tests.
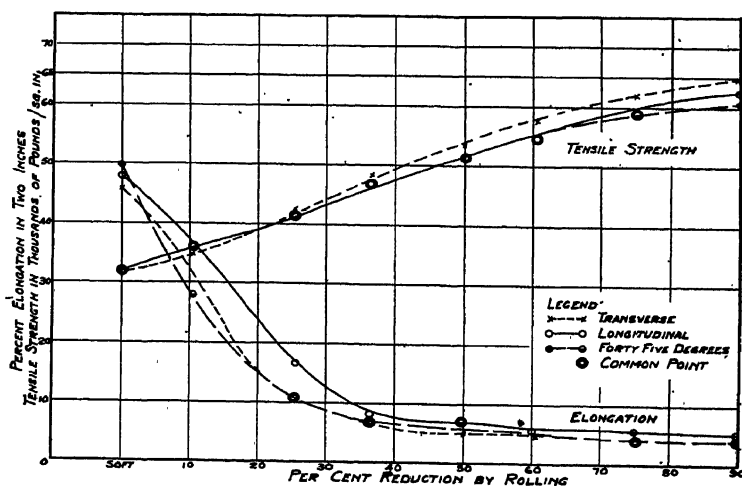
FIG. 1.—DIRECTIONAL PROPERTIES OF ROLLED COPPER (TOUGH-PITCH LAKE).

interesting, and perhaps surprising, results of this series of tests is the relatively slight difference in tensile properties of the three kinds of test specimens, even after very heavy reductions.   In both kinds of copper, at about 35 per cent. reduction there are divergences between the transverse tests which are the highest, and the almost identical curves of the other two types.   At the highest reduction, 90 per cent., the transverse strength of the tough-pitch lake copper is approximately 3 per cent. greater than that of the longitudinal and about 6.5 per cent. greater than the 45° strips.   The differences in the deoxidized copper are essentially the same; namely, 4.5 and 6.5 per cent.   These ratios are significant
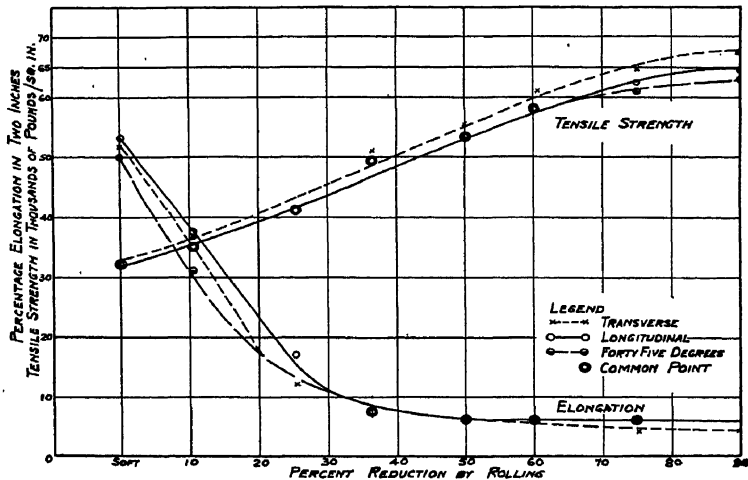
FIG. 2.—DIRECTIONAL PROPERTIES OF ROLLED COPPER (DEOXIDIZED).

in that they indicate that cuprous oxide, in the amount present in the tough-pitch copper, forms too little fiber to influence appreciably the directional properties of the copper.   With respect to the elongation values, there are rather marked differences between the three kinds of test bars after the lower reductions.   After reductions of 30 to 40 per cent. in both coppers, the curves of the three kinds of strips run close together.   In general, however, beyond this point the longitudinal pieces yielded slightly, but consistently, higher values.   Although it may be considered that the differences are too small to justify the statement that the longitudinal direction gives greater elongation, the results clearly indicate, at least, that the values in the three directions are essentially the same after the heavier reductions.

TESTS ON ANNEALED COPPER

The next series of experiments consisted of testing annealed pieces cut in the three directions from the original rolled sheets.   In other

words, the annealing program adopted makes it possible to compare the relative effects of heavy reductions followed by low annealing tempera-

TABLE 4.—*Tensile and Hardness Values of Annealed Copper*[a]
(Tough-pitch Lake)

Temperature of Anneal, Deg. C.	Test Specimens Cut Parallel to Direction of Rolling		Test Specimens Cut at Right Angles to Rolling Direction		Test Specimens Cut 45° to Direction of Rolling		Rockwell Hardness, ⅟₁₆-in. Ball, 100-kg. Load, B Scale
	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Por Cent. in 2 In.	
PREVIOUSLY REDUCED 10.5 PER CENT.							
300	35,850	34.2	34,450	33.	34,300	31.5	81.5
400	32,400	51.2	31,600	42.5	31,500	51.5	30.
500	31,700	49.5	31,425	52.5	30,900	51.	24.5
600	31,500	49.5	31,300	51.5	30,900	53.2	22.
700	31,600	49.5	31,250	50.5	30,900	51.5	18.70
800	31,400	50.5	30,150	48.7	30,200	49.5	17.
PREVIOUSLY REDUCED 25.5 PER CENT.							
300	40,775	16.5	42,275	9.5	41,025	11.2	90.
400	32,300	52.2	32,000	41.7	32,350	53.5	33.
500	31,725	51.1	31,575	53.5	31,425	52.4	27.2
600	31,675	51.7	31,650	53.7	31,475	52.2	24
700	31,500	51.	31,550	53.	31,525	54.	19.7
800	31,250	47.5	31,325	46.5	30,950	51.5	18.2
PREVIOUSLY REDUCED 36.4 PER CENT.							
300	47,100	10.	48,450	6.3	46,625	8.6	94.5
400	33,150	50.7	32,700	53.7	32,800	53.7	36.5
500	31,875	53.6	31,925	53.5	31,925	54.3	30.1
600	32,050	52.5	31,700	53.	31,700	53.8	25.8
700	31,825	51.	31,600	51.7	31,700	57	21.7
800	31,500	50.	31,150	48.50	31,200	54.3	17.1
PREVIOUSLY REDUCED 50 PER CENT.							
300	49,425	9.7	50,250	6.6	48,950	7.3	95.6
400	33,150	52.	32,875	53.7	32,400	55.5	38.6
500	32,425	51.7	32,275	54.5	31,750	57.5	30.1
600	31,375	52.5	31,750	57.5	31,400	54.8	25.
700	31,325	52.	31,575	54.5	31,050	54.2	20.1
800	30,750	51.	30,750	53.6	30,225	57.3	19.

[a] Values are average of three tests.

tures with light reductions and high-temperature anneals. The three kinds of strip, in duplicate, were annealed for 30 min. at every 100°

between 300° and 800° C. inclusive. This plan required the annealing and testing of 650 pieces, not including a few additional tests which were necessary for checking certain determinations. The complete testing

TABLE 5.—*Tensile and Hardness Values of Annealed Copper*[a]
(Tough-pitch Lake)

Temperature of Anneal, Deg. C.	Test Specimens Cut Parallel to Direction of Rolling		Test Specimens Cut at Right Angles to Rolling Direction		Test Specimens Cut 45° to Direction of Rolling		Rockwell Hardness, ⅛-in. Ball, 100-kg. Load, B Scale
	Tensile Strength, Lb. per Sq. In.	Elonga-tion, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elonga-tion, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elonga-tion, Per Cent. in 2 In.	
PREVIOUSLY REDUCED 60.5 PER CENT.							
300	53,700	6.1	56,325	5.2	53,850	5.5	99.1
400	36,750	51.5	33,400	53.5	32,850	53.7	49
500	32,500	53	32,300	51.7	31,800	55	39.1
600	32,150	48.5	31,900	54	31,400	56	25.6
700	32,300	49.5	31,500	51.5	31,200	54.8	13.5
800	31,900	45.7	31,350	50.7	30,625	54	6.7
PREVIOUSLY REDUCED 75.1 PER CENT.							
250	54,000	7.5	55,500	5	51,500	6	
300	35,300	43.5	34,650	49	33,900	52	54
400	33,750	50.5	33,350	52.6	32,750	55	43.5
500	31,300	49	32,400	52	31,600	54.7	33.2
600	31,300	50	31,650	53.30	30,650	56	27
700	31,550	50.2	31,275	53	30,550	62.2	24.8
800	30,000	49.5	29,500	52	28,600	58.8	22.5
PREVIOUSLY REDUCED 89.8 PER CENT.							
250	56,000	7.5	57,500	6	54,000	7.5	
300	34,150	47.7	33,000	47	32,400	53.5	51
400	32,550	49	31,850	50.5	31,250	60.7	42.6
500	31,050	48.5	30,300	49.5	29,900	61.5	32.2
600	29,900	49.3	29,250	48.5	29,250	64.2	26.5
700	28,850	46.5	28,450	45	28,325	68.5	22
800	26,200	41.2	26,250	42	26,950	76.5	16.5

[a] Values are average of three tests.

data are compiled in Tables 4 and 5 for the tough-pitch copper and Tables 6 and 7 for the phosphorized copper. In order that there may not be too many of the characteristic curves, only the results of the annealing experiments on three reductions are included; namely, 36.4, 60.5 and 89.8 per cent. (Figs. 3 to 8 inclusive.)

The annealing curves are similar in form to the curves found in the literature on copper.   In general, they consist of three parts: (1) a tem-

TABLE 6.—*Tensile and Hardness Values of Annealed Copper*[a]
(Deoxidized Electrolytic)

Temperature of Anneal, Deg. C.	Test Specimens Cut Parallel to Direction of Rolling		Test Specimens Cut at Right Angles to Rolling Direction		Test Specimens Cut 45° to Direction of Rolling		Rockwell Hardness, 1/16-in. Ball, 100-kg. Load, B Scale
	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	
PREVIOUSLY REDUCED 10.5 PER CENT.							
300	36,950	32.2	35,800	34.7	36,225	36.7	86
400	36,150	37.2	34,825	39.7	35,350	39.5	80
500	32,800	56.7	32,500	55.00	32,775	55.5	30
600	32,425	53.2	32,600	50.2	32,150	53.2	23
700	32,450	54.5	32,250	56.5	32,025	51.7	17.5
800	30,750	39	30,125	43.7	30,675	39.7	3
PREVIOUSLY REDUCED 25.5 PER CENT.							
300	40,200	24.5	40,850	15.7	40,300	16	90
400	37,100	34	36,350	37.00	36,200	39	80
500	32,700	52	32,800	54	32,775	53	31.7
600	32,775	53.5	32,675	52	32,650	54.2	26
700	32,350	53.5	32,100	53.5	31,875	51	17.6
800	31,050	46.7	31,125	48.7	30,325	50.5	4
PREVIOUSLY REDUCED 36.4 PER CENT.							
300	48,700	9.7	49,600	11	47,925	9.2	96.20
400	34,750	48	34,350	48.7	34,500	49	46.5
500	33,250	52.5	33,250	54.00	32,950	52.7	34
600	33,175	51.10	33,150	53.5	32,600	54	27
700	31,725	49	31,650	55	31,500	55	12.5
800	31,600	47.5	30,800	51.2	30,600	51.7	5
PREVIOUSLY REDUCED 50 PER CENT.							
300	49,200	10.50	50,900	9.2	48,550	10.7	96.5
400	34,000	52	33,950	49.50	33,750	54	45.5
500	33,400	53.5	32,900	55.5	33,350	55	35
600	33,300	57	32,500	56.2	33,075	53	26.5
700	32,000	55.5	31,950	57.7	31,650	56.2	13.4
800	31,625	50.2	30,000	54.50	31,150	52.2	7.2

[a] Values are average of three tests.

perature range, below the recrystallization temperature, in which the three kinds of strip maintain substantially the relative positions inherited

from the rolling treatment, (2) an extremely narrow temperature range
in which a marked change in properties occurs and (3) a temperature
range extending from the recrystallization temperature up to 800°.
Since the last portion of the curves includes the annealing temperatures

TABLE 7.—*Tensile and Hardness Values of Annealed Copper*[a]
(Deoxidized Electrolytic)

Temperature of Anneal, Deg. C.	Test Specimens Cut Parallel to Direction of Rolling		Test Specimens Cut at Right Angles to Rolling Direction		Test Specimens Cut 45° to Direction of Rolling		Rockwell Hardness, ⅟₁₆-in. Ball, 100-kg. Load, B Scale
	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	
PREVIOUSLY REDUCED 60.5 PER CENT.							
300	55,900	7	58,875	6	56,000	6.3	99.2
400	35,750	47.5	35,150	52.5	35,300	52.5	49
500	34,400	53.5	33,850	55.5	33,700	53	39
600	34,000	50.5	32,700	57.3	32,650	55	25.5
700	33,675	50	31,350	54.2	31,100	54.5	13.4
800	32,350	46	30,400	51	30,000	56	6.6
PREVIOUSLY REDUCED 75 PER CENT.							
200	62,500	6	64,500	3.5	61,000	6	
300	55,900	10.5	56,900	10.30	53,900	11	99.6
400	36,550	48.5	35,300	51.5	35,000	53.7	51.2
500	36,050	48.3	34,250	52.7	34,450	55	43.5
600	35,150	48.5	32,500	55.7	32,000	56	26.5
700	34,950	45.7	31,100	57.7	30,100	56	12.6
800	35,150	42.2	30,600	58	29,250	54.7	7.8
PREVIOUSLY REDUCED 89.8 PER CENT.							
200	64,400	5.7	67,350	4	63,000	5	101
300	58,950	10.5	59,800	8	55,800	7.8	100
400	37,450	47.5	35,750	51.2	35,550	52.2	57
500	36,950	49.2	34,300	52.3	34,700	52.5	49
600	35,750	48	33,100	56.5	33,100	54.5	36.5
700	35,450	46.7	31,200	59	30,600	55.2	18.7
800	35,500	42.7	30,750	59.5	29,200	55	8

[a] Values are average of three tests.

commonly used in mill heat treatment, the discussion will be limited to
this range.   Considering first the curves denoting the strength values
of the annealed tough-pitch copper, we find little difference in the strength
of the three strips; no one direction can be considered to possess marked
superior strength properties.   In the deoxidized copper, there are notice-

able differences in the strength values of the three strips after the anneals following the higher reductions, more specifically after reductions from
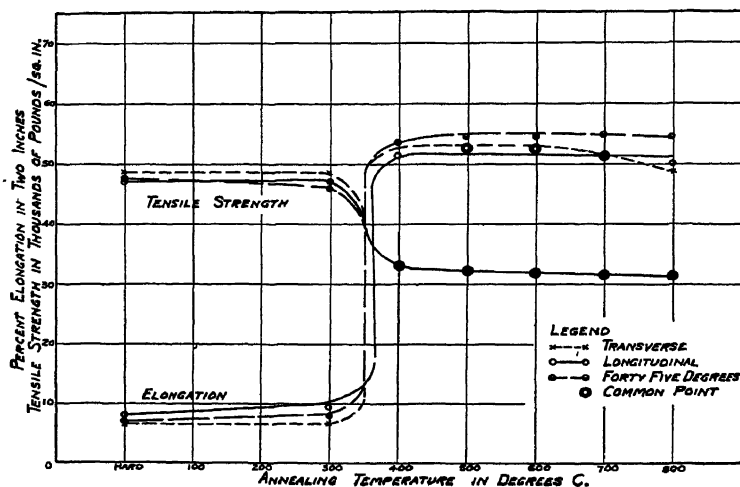
FIG. 3.—DIRECTIONAL PROPERTIES OF ANNEALED COPPER (TOUGH-PITCH LAKE. PREVIOUS REDUCTION 36.4 PER CENT.).

60 to 90 per cent.; furthermore, the differences become more pronounced as the temperature of anneal is raised.   The strength in the direction of
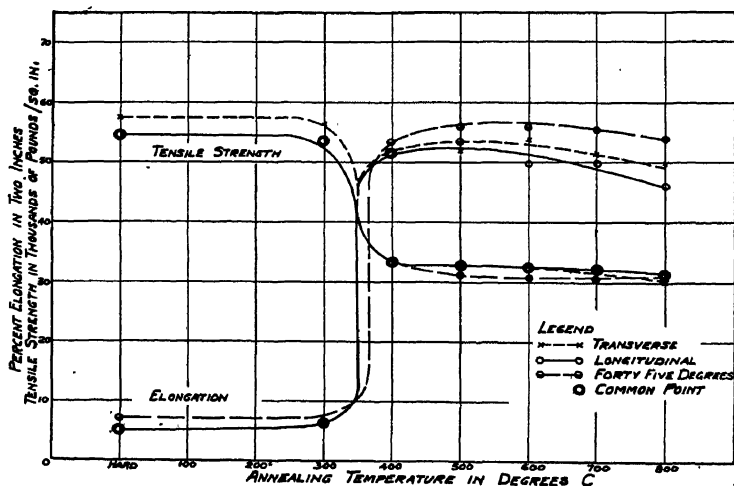
FIG. 4.—DIRECTIONAL PROPERTIES OF ANNEALED COPPER (TOUGH-PITCH LAKE. PREVIOUS REDUCTION 60.5 PER CENT.).

rolling is the greatest, with the transverse and 45° directions following in the order named. It is interesting to note that after anneals at the

highest temperature, after reductions of from 75 to 90 per cent., the
strength of the longitudinal strip is approximately 20 per cent. greater
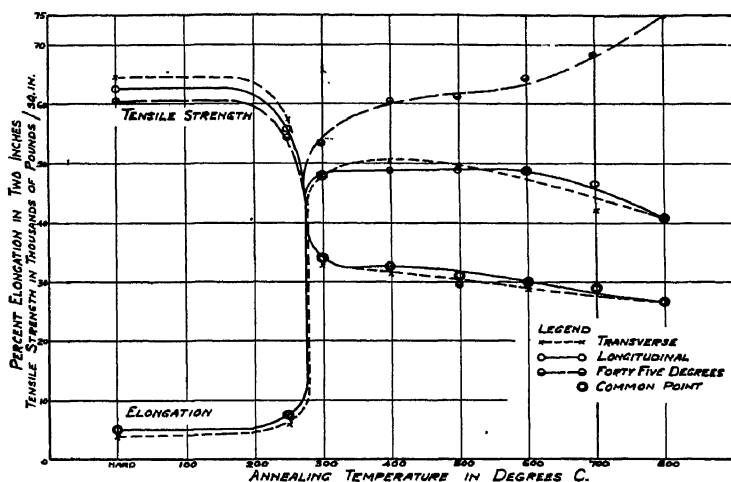
FIG. 5.—DIRECTIONAL PROPERTIES OF ANNEALED COPPER (TOUGH-PITCH LAKE
PREVIOUS REDUCTION 89.8 PER CENT.).

than that cut at 45° to the axis of rolling. This directional difference is
considerably greater than in the hardest rolled sheets tested in the first
series of experiments.
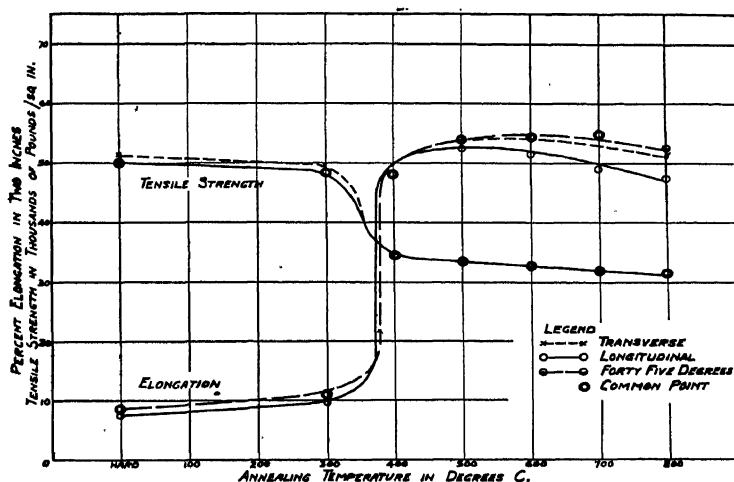
FIG. 6.—DIRECTIONAL PROPERTIES OF ANNEALED COPPER (DEOXIDIZED. PREVIOUS
REDUCTION 36.4 PER CENT.).

Considering next the elongation values, in both types of copper after
heavy reductions and high annealing temperatures, we note unquestion-

have been encountered.   Further work on the effect of the "get ready" anneal is now being planned and it is hoped that additional data on this subject will be obtained in the near future.

DISCUSSION

(Sam Tour presiding)

W. B. Price, Waterbury, Conn. (written discussion).—This paper would have been more conclusive and valuable had the authors included a tough-pitch lake copper deoxidized with phosphorus, so that the silver content would have been the same. They say that they "are aware that it is not permissible to compare the properties of silver-bearing copper and electrolytic copper, or electrolytic copper treated with phosphorus.   The purpose was merely to compare the directional properties of copper containing its impurities in solid solution and to make the same observations on a second type of copper containing cuprous oxide as a mechanical mixture capable of being extended into a visible, though discontinuous, fiber."   Their purpose would have been as well served by deoxidizing a tough-pitch lake copper.   The tough-pitch lake copper used contained 9.45 oz. per ton of silver, and silver has a very decided effect on the properties of copper, not only raising the initial annealing point but also affecting the tensile strength and Rockwell values.

We have replotted some of the tensile strength and Rockwell values given on pages 360 to 363 on specimens cut parallel to the direction of rolling, on the tough-pitch lake and deoxidized electrolytic copper annealed at 500° and 800° C., plotting tensile strength and Rockwell values against percentage reduction by rolling prior to the anneal.

It is evident that the tensile strength and hardness values of the deoxidized electrolytic copper increase with the percentage reduction by cold-rolling prior to annealing (Fig. 9).   This could be explained on the basis of the well-established law that the more severely a metal is worked the finer the crystal size after annealing, if it were not for the fact that the hardness and tensile strength values for tough-pitch lake copper do not show similar increases (Fig. 10).   In fact, the tensile strength values for the metal annealed at 800° C. decrease pronouncedly with the higher reductions.   A possible explanation of this rests on the assumption that self-annealing might have taken place during rolling, since the tough-pitch lake copper has a lower recrystallization temperature than the deoxidized electrolytic.   However, the data in Table 3 tend to contradict this idea, for the hardness and strength values of the tough-pitch lake copper increase progressively with the reduction by cold-rolling.

Upon comparing the Rockwell hardness curves, it was found that the values for the deoxidized electrolytic specimens annealed at 800° C. were much lower than those obtained on the tough-pitch lake specimens in spite of the fact that the tensile strength values (at least after the higher reductions) were just the reverse.   On the other hand, the Rockwell curves on the specimens annealed at 500° C. seem to parallel the tensile strength curves in a normal fashion.

It seems probable that the discordant Rockwell values obtained on the 800° C. specimens were due to differences in the surfaces of the specimens used. It has been demonstrated[9] that tough-pitch and phosphorized copper scale differently above
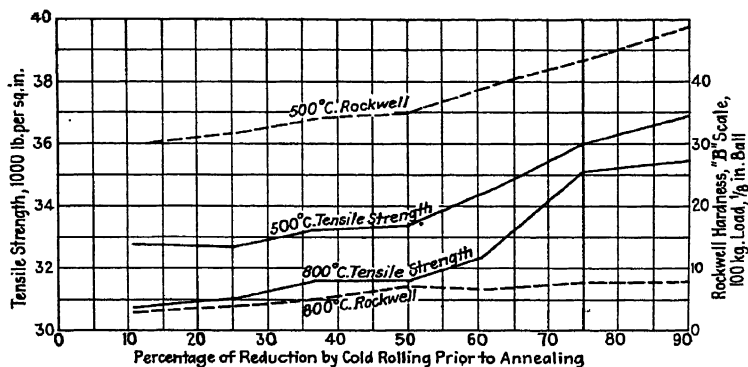
FIG. 9.—TENSILE STRENGTH AND HARDNESS OF DEOXIDIZED ELECTROLYTIC COPPER ANNEALED AT 500° AND 800° C. AFTER PROGRESSIVE REDUCTIONS BY COLD ROLLING. Test specimens cut parallel to direction of rolling.
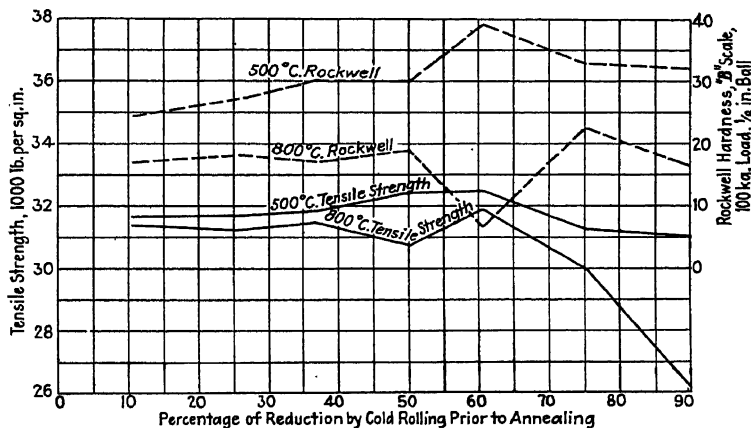
FIG. 10.—TENSILE STRENGTH AND HARDNESS OF TOUGH-PITCH LAKE COPPER ANNEALED AT 500° AND 800° C. AFTER PROGRESSIVE REDUCTIONS BY COLD ROLLING. Test specimens cut parallel to direction of rolling.

750° C. If the specimens were prepared for testing merely by pickling it is not surprising that different surface hardness values were obtained.

The divergence of the tensile strength curves, however, cannot be explained away so simply and seems to show a basic difference in the two kinds of copper.

R. S. PRATT, Bridgeport, Conn. (written discussion).—At about the same time that Phillips and Bunn started their work on copper, we began a similar set of tests on high-grade 67:33 sheet brass. The program was practically identical with that outlined in the paper and was based on some previous experiments which indicated that tests

[9] W. R. Webster, J. L. Christie and R. S. Pratt: Some Comparative Properties of Tough-pitch and Phosphorized Copper. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 323.

with, across and at 45° to the direction of rolling would furnish direct evidence as to the relation of final reduction and annealing temperatures to the development of ears. Many interesting data were obtained, but unfortunately no clear-cut evidence of this nature was found. It has been felt since that many of the variations in directional properties from what had been expected were due to variations in the details of the history of the individual samples.

In general, the tests developed the presence of tendencies in the annealed material similar to those shown in the paper for copper. The maximum elongations were found in the specimens cut at 45° to the direction of rolling, with the minimum elongations in the parallel samples. Maximum tensile strengths were generally found in the parallel samples, with minimum tensile strengths in the 45° samples. While the greatest variation in directional properties occurred as in copper, after the greatest reductions and highest annealing temperatures, the extent of these variations apparently is not as great under the same conditions. This difference indicates, and practical experience bears out, the fact that copper is more susceptible to the formation of ears than is high brass.

These tests and others on commercial cases of the formation of ears indicated that tensile tests could not always be interpreted well enough to forecast the formation of ears in the cupping press. For this reason some additional tests were made on the same materials rolled down to sizes convenient for trial in the cupping press. Samples rolled 4 and 16 numbers hard were annealed at various temperatures and tried out in the press. Ears could be obtained only with heavier reduction by annealing so as to produce a grain size coarser than that produced by the anneal previous to the final reduction. While this point has not been confirmed as yet, it checks a portion at least of the conclusions brought out by Kaiser in 1928, in a paper on the development of ears in copper, in which he states that a final annealing temperature higher than the next to last annealing temperature, following reductions of over 70 per cent, tends to cause ears on cupping.

It is apparent that there are a number of factors other than the degree of final reduction and the final annealing temperature. The work that we have done would indicate that a study of the relation of the last two annealing temperatures and the intermediate reduction may show why it is that noticeable ears are obtained occasionally in material that has been rolled only 4 to 6 numbers before the final anneal.

C. H. BENEDICT, Lake Linden, Mich. (written discussion).—Without any bearing on the accuracy of the experimental results, and with full recognition of the value of the work, I wish to direct attention to Table 1. According to the author, this chemical work was done by the Nichols Copper Co., and there is either a typographic error or a decided contamination of the lake copper. Prime lake copper does not contain lead or antimony, although it has occasionally been accused of harboring one or both. The two analyses given, except for copper, silver, oxygen and phosphorous content, show a similarity so striking as to suggest possible reagent contamination.

F. F. POLAND, Baltimore, Md.—We have made a number of analyses of prime lake copper in the laboratory of the Baltimore Copper Smelting & Rolling Co., and have found from 0.0002 to 0.0009 per cent. antimony. Bassett and Davis have reported an analysis of high-grade lake copper showing 0.0026 per cent. antimony.[10]

H. C. KENNY, Hubbell, Mich.—The Calumet & Hecla smelter has been making analyses of lake copper for a great many years and has never yet detected the presence of antimony. These results have been checked by reliable authorities. An exhaus-

[10] W. H. Bassett and C. H. Davis: Physical Characteristics of Commercial Copper-zinc Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 57.

tive investigation is now being carried out on this subject, which will be reported on shortly, but nothing has been found so far to make us change our stand.   Mr. Poland may remember that when he visited the smelter about two years ago he promised to send us a sample of lake copper containing antimony, but so far we have not received it.

D. K. CRAMPTON, Marion, Conn. (written discussion).—We wish merely to direct attention to the last paragraph on page 367, where the authors state their belief that differences in preliminary history of the material might considerably modify the results obtained.   Our experience with rolling and fabricating of sheet brasses and copper leads us to believe that this is most certainly the case.   We wish to raise the question of whether these directional effects may not be, partially at least, of a cumulative nature and whether operations well back from the finishing ones might have a pronounced effect on the finished product in this respect.   It would seem that a complete study of the question would necessarily involve studies of these intermediate operations.

K. R. VAN HORN, Cleveland, Ohio (written discussion).—A paper of this nature, which deals with the anisotropic properties of metals, is of vital interest to the metallurgist.   The study of directional tendencies of metals has received relatively little attention in America and this paper is well timed.

There are a number of discrepancies between the results of directional studies in brass and copper sheet recorded in the literature and in the present discussion. Perhaps a true evaluation of the type of fibering influencing the mechanical properties in a particular investigation might explain some of the discordant results.

In a cold-worked, pure metal possessing no mechanical fibering,[11] the directional properties probably could be attributed to a preferred orientation of the individual crystallites.   The authors found that the transverse (perpendicular to the direction of rolling) tensile strength was greater than the longitudinal (parallel to the rolling direction) strength of deoxidized cold-rolled copper sheet.   These results and previous publications on cold-rolled high-purity copper sheet would indicate that the preferred grain arrangement is such that the greatest tendency for slip and consequent inferior strength is parallel to the direction of rolling.

If mechanical fibering were also present in the cold-rolled copper sheet, it would tend to cause longitudinal planes of weakness and thereby decrease the transverse tensile strength.   The effect of the mechanical fiber and crystallographic alignment or fibering of the grains in cold-rolled copper sheet would therefore be compensating and it would be possible to have copper sheet possessing either superior transverse or longitudinal tensile properties, depending on the type and magnitude of the fiber present.   Phillips and Bunn show that the mechanical fibering of the copper oxide in the tough-pitch specimens decreased the more pronounced directional transverse tendencies characteristic of the deoxidized copper.   The compensating effect of the two types of fiber might explain some of the results cited in the discussion.

The conditions mentioned above are characteristic only of cold-rolled copper, or perhaps any face-centered cubic metal sheet.   In forged or pressed products of a face-centered cubic metal, the type of preferred grain arrangement is entirely different. The crystalline grains are so oriented that the longitudinal (parallel to the direction of forging) tensile properties are superior to the transverse.   The effect of a mechanical fiber in the direction of forging and the preferred grain orientation would be cumulative in this case.

Some very interesting results of directional studies of metals are incorporated in a thesis on the Strength and Angle of Shear of Cold-rolled Metals presented at the Technische Höchschule in Aaken, Germany, by F. Körber and H. Hoff.   They investi-

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[11] The elongation of metallic and nonmetallic inclusions, impurities, blowholes and shrinkage cavities in the direction of working.

gated a number of metals reduced 70 to 98 per cent. by cold rolling and measured the tensile properties of specimens cut parallel, at 22.5°, 45°, 67.5° and perpendicular to the direction of rolling.   For pure copper, they found that the transverse tensile strength exceeded the longitudinal by 5 per cent. and observed the tensile strength minimum at 45° to the direction of rolling, which closely checks the results of Phillips and Bunn. Cold-rolled aluminum sheet yielded practically isotropic results but the copper alloys exhibited marked directional tendencies.   In cold-rolled sheet of alpha brass and the German gilding alloy, Tomback (85 per cent. Cu, 15 per cent. Zn), the transverse tensile strengths were 20 per cent. greater than the longitudinal.   Perhaps the introduction of the zinc atoms in the alpha solid solution has exaggerated the original directional properties due to a preferred grain arrangement of pure copper sheet?

Fundamental investigations of the effect of mechanical and crystallographic fibering on the tensile properties of worked metals and alloys should prove a valuable contribution to the science of metallography.

A. PHILLIPS (written discussion).—We agree with Mr. Price that it is unfortunate that the experimental results of this paper cover two kinds of copper.   As a matter of fact, we had planned to use standard electrolytic copper and electrolytic copper deoxidized with phosphorus.   After the copper had been received it was found that, through an error, lake copper had been substituted for electrolytic.   This substitution, however, was not deemed serious, as the original intention was to study the directional properties in a given kind of copper and not to make direct comparisons of the properties of deoxidized and undeoxidized copper.

We are unable to explain the downward trend of Rockwell hardness curve for the deoxidized electrolytic copper.   Since the receipt of Mr. Price's suggestion that the character of the surface might account for the seemingly inconsistent results, we have repeated the hardness tests after a thorough preparation of the surfaces of the original specimens.   The second determinations were in excellent agreement with the values stated in the paper.

It is pleasing to note that Mr. Pratt's work on the directional properties of 67: 33 sheet brass yielded results differing only in degree from our work on copper.   We are particularly interested to observe that he found the greatest directional differences after the greatest reductions and the highest annealing temperatures.   Mr. Pratt probably is correct in believing that the last two anneals and the intermediate reduction are important in considering the causes of earing.   We are inclined to go beyond this point, however, and to agree with Mr. Crampton that the directional properties may be of a cumulative nature and that a thorough study of the history of the metal may be necessary, in many instances, to explain the directional effects commonly noted.

We are interested in Mr. Van Horn's remarks regarding the possible compensating effects of mechanical fiber and the type of fiber resulting from preferred orientations.   The unpublished work of Körber and Hoff, to which our attention has been drawn by Mr. Van Horn, apparently checks our work on cold-rolled copper.

Messrs. Benedict, Poland and Kenny showed interest in the question of whether or not prime lake copper contains antimony.   We have little to contribute to this angle of the discussion.   We are indebted, however, to Mr. Fitzpatrick of the Nichols Copper Co. for a recheck on the antimony content, and he has assured us that the original determination was correct.   It is possible, of course, that the tough-pitch lake copper was a mixture of lake and some other copper.

Effect of Combinations of Strain and Heat Treatment on Properties of Some Age-hardening Copper Alloys

By W. C. Ellis* and Earle E. Schumacher,* New York, N. Y.

For the purpose of developing combinations of higher strength and conductivity than are obtainable by heat treatment alone in the age-hardening copper alloys, an investigation has been made of the effects of combinations of heat treatment and strain hardening on the properties in question. The investigation was limited to a study of the alloys containing nickel and silicon; nickel, silicon and cadmium; and cobalt and silicon. The experiments made in the course of the study are described in this paper in three groups:

1. The effect of hard drawing subsequent to heat treatment on the mechanical and electrical properties of the alloys.

2. The effect of low-temperature aging on the properties of heat-treated and hard-drawn alloys.

3. The effect of strain on the rate of aging of quenched nickel-silicon-copper alloys.

Preparation and Compositions of the Alloys

The alloys were prepared by melting cathode copper in an electric resistance furnace and adding sufficient of the hardening elements to

TABLE 1.—*Compositions of Hardenable Copper Alloys Investigated*

Alloy No.	Cu	Ni	Co	Si	Cd
1	Balance	2.8		0.55	
2	96.2	3.1		0.75	
3	94.8	4.1		0.93	
4	Balance	4.7		0.92	
5	92.5	6.1		1.10	
6	94.2	4.1		0.71	0.80
7	Balance		0.94	0.27	
8	96.6		2.60	0.63	

bring the compositions to the desired values. The purities of the hardening elements were as high as could be obtained in commercial practice. The metals were what are designated in the trade as electrolytic nickel, cobalt rondelles, commercial stick cadmium and fused silicon. The alloys

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* Members of Technical Staff, Bell Telephone Laboratories.

were cast into 0.750-in. round bars which were subsequently hot-rolled to 0.250-in. rod. This rod was then drawn to the size desired for heat treatment. All of the tests were made on material in wire form. The alloys that were included in the investigation, together with the compositions by analysis, are listed in Table 1.

Effect of Hard Drawing Subsequent to Heat Treatment on Mechanical and Electrical Properties of Alloys

In this series of experiments, the alloys were drawn to wires of 0.100 in. dia. The wires were heat-treated and then drawn further to a diameter of 0.045 in. For No. 2 alloy, the heat-treated and final sizes were, respectively, 0.090 in. and 0.040 in. dia. The reduction by drawing in both cases was approximately 80 per cent.
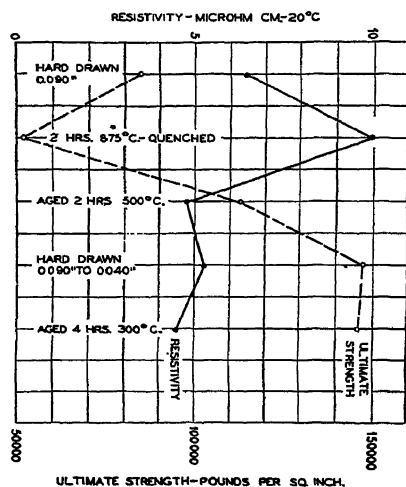
FIG. 1.
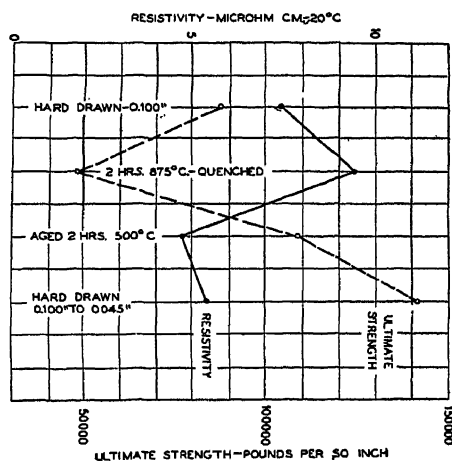
FIG. 2.

FIG. 1.—EFFECT OF HEAT TREATMENT AND MECHANICAL STRAIN ON PROPERTIES OF HARDENABLE COPPER ALLOY CONTAINING 3.1 PER CENT. NI AND 0.75 PER CENT. SI.

FIG. 2.—EFFECT OF HEAT TREATMENT AND MECHANICAL STRAIN ON PROPERTIES OF HARDENABLE COPPER ALLOY CONTAINING 4.1 PER CENT. NI AND 0.93 PER CENT. SI.

The mechanical and electrical properties of the several alloys were determined after each stage of the heat treatment and after the drawing. Charts illustrating the change of the properties of the wires during the heat treatment and drawing are shown in Figs. 1 through 4 for representative alloys containing the nickel-silicide hardener. Figs. 5 and 6 give the same data for the two alloys containing cobalt and silicon. The results for the complete series are summarized in Table 2.

A consideration of the data for the copper-nickel-silicon alloys shows that the heat-treated wires were strengthened considerably by subsequent drawing without much sacrifice in conductivity. The maximum

strengths and resistivities developed in alloys containing different nominal percentages of nickel plus silicon are plotted in Fig. 7. This figure shows that an increase of the nickel plus silicon content above 4 per
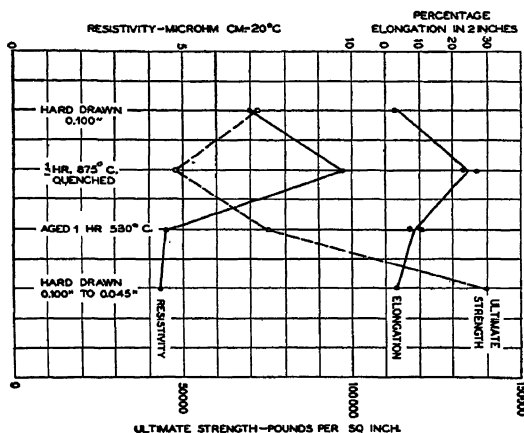
FIG. 3.—EFFECT OF HEAT TREATMENT AND MECHANICAL STRAIN ON PROPERTIES OF HARDENABLE COPPER ALLOY CONTAINING 4.7 PER CENT. NI AND 0.92 PER CENT. SI.

cent. does not materially affect either the tensile strength or the conductivity under the conditions of treatment used in this study. In this range the increase of tensile strength that results from hard drawing is approximately 35,000 lb. per square inch.
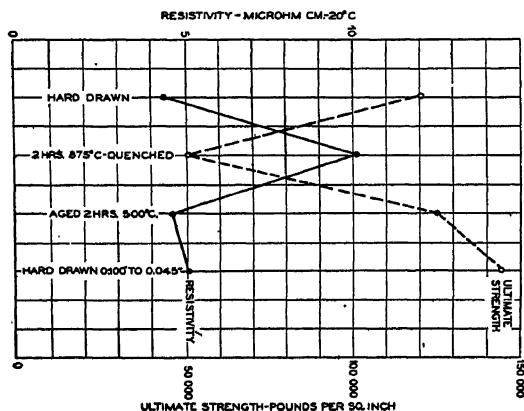
FIG. 4.—EFFECT OF HEAT TREATMENT AND MECHANICAL STRAIN ON PROPERTIES OF HARDENABLE COPPER ALLOY CONTAINING 4.1 PER CENT. NI, 0.57 PER CENT. SI AND 0.80 PER CENT. CD.

The effect of cadmium on the properties of the copper-nickel-silicon system was investigated with alloy No. 6. Cadmium was chosen because it is well known that copper is strengthened by the addition of this

element without much loss in conductivity, while presumably the resulting alloy is a solid solution. It was thought that increased strengths might result from dispersion hardening in this solid solution. A pre-
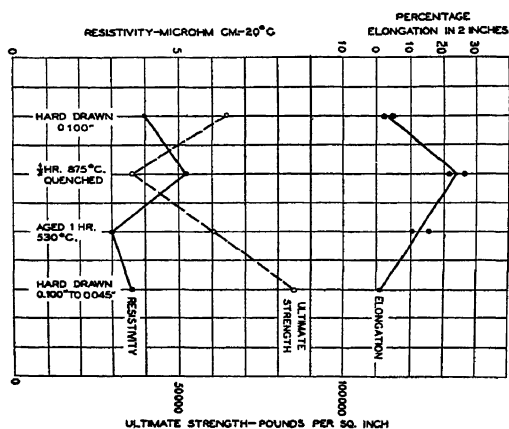
FIG 5.
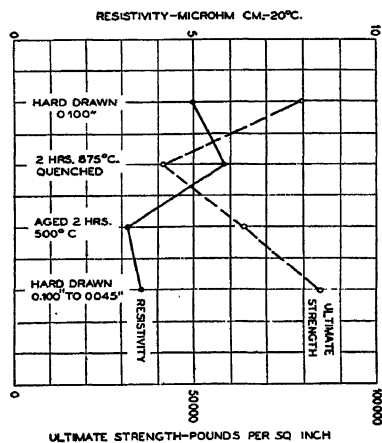
FIG. 6.

FIG. 5.—EFFECT OF HEAT TREATMENT AND MECHANICAL STRAIN ON PROPERTIES OF HARDENABLE COPPER ALLOY CONTAINING 0.94 PER CENT. CO AND 0.27 PER CENT. SI.
FIG. 6.—EFFECT OF HEAT TREATMENT AND MECHANICAL STRAIN ON PROPERTIES OF HARDENABLE COPPER ALLOY CONTAINING 2.6 PER CENT. CO AND 0.63 PER CENT. SI.

liminary investigation, by means of a hardness survey, of the optimum conditions of heat treatment showed that the aging characteristics of this alloy were essentially the same as those of copper containing the same percentage of dispersion hardener. The effect of optimum heat treat-
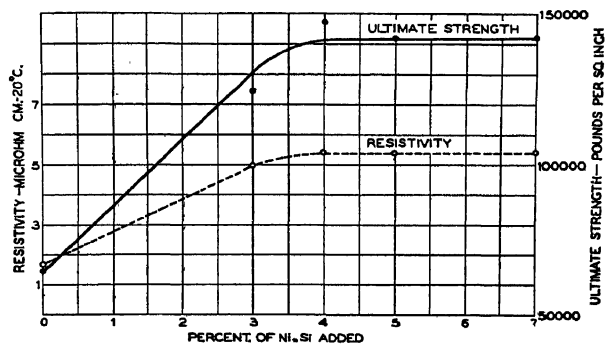
FIG. 7.—EFFECT OF NOMINAL Ni_2Si CONTENT ON STRENGTH OF HARDENABLE COPPER ALLOYS IN HEAT-TREATED AND HARD-DRAWN CONDITION.

ment together with subsequent drawing is shown in Fig. 4. The tensile strength obtained after heat treatment of this alloy was approximately 10,000 lb. per sq. in. higher than with the corresponding nickel-silicon-

copper alloy. The increase after drawing was somewhat less, however, resulting in a final strength which was approximately the same as was obtained with the simpler alloy. There is the possibility, however, that a different percentage of reduction by drawing might give materially higher tensile properties.

The copper alloys containing cobalt and silicon showed the same general characteristics in the heat-treated and drawn condition as the copper-nickel-silicon alloys previously considered. These characteristics are illustrated in Figs. 5 and 6. The tensile strength was increased by drawing approximately 25,000 lb. per sq. in. The maximum strength in this case was but 85,000 lb. per sq. in. associated with a conductivity of approximately 50 per cent. of that of annealed copper. These facts make the alloys containing cobalt of interest in applications requiring relatively low strength associated with a conductivity somewhat higher than that obtainable in the copper-nickel-silicon system by the same treatment. Table 2 shows that no increase in strength resulted from increasing the cobalt plus silicon content above 1 per cent. This is not in agreement with data published by Corson[1] in which the strength of heat-treated and cold-rolled material increased progressively with

[1] M. G. Corson: Copper Alloy Systems with Variable Alpha Range, and Their Use in the Hardening of Copper. *Proc.* Inst. Metals Div., A. I M. E. (1927) 435.

TABLE 2.—*Effect of Heat Treatment and Hard Drawing on Properties of Hardenable Copper Alloys*

Alloy No.	Composition, Per Cent.					Heat-treated			Heat-treated and Hard-drawn		
	Cu	Ni	Co	Si	Cd	Wire Size, In.	Ultimate Strength, Lb. per Sq. In.	Resistivity, Microhm Cm. at 20° C.	Wire Size, In.	Ultimate Strength, Lb. per Sq. In.	Resistivity, Microhm Cm. at 20° C.
1	Bal.	2.8		0.55		0.100	68,000	4.2	0.045	125,000	5.0
2	96.2	3.1		0.75		0.090	113,000	4.8	0.040	148,000	5.3
3	94.8	4.1		0.93		0.100	109,000	4.7	0.045	141,000	5.4
4	Bal.	4.7		0.92	0.80	0.100	75,000	4.5	0.045	140,000	4.4
5	92.5	6.1		1.10		0.100	114,000	4.8	0.045	142,000	5.3
6	94.2	4.1		0.57		0.100	125,300	4.8	0.045	144,000	5.1
7	Bal.		0.94	0.27		0.100	61,000	3.0	0.045	85,000	3.6
8	96.6		2.60	0.63		0.100	64,000	3.2	0.045	85,000	3.6

content of Co_2Si in the range from 1 to 3 per cent.   This difference may be due to variations in condition of heat treatment in the two cases.

In the course of the investigation, the end properties of the alloys were observed to depend to some extent upon the conditions of heat treatment.   In Fig. 3 is shown the change of properties of an alloy containing a nominal 5 per cent. of nickel plus silicon, during heat treatment in which the aging was carried out at 530° C. for 1 hr.   This aging was for a shorter time at a higher temperature than with alloy No. 3, illustrated in Fig. 2.   A comparison of Figs. 2 and 3 shows that interesting differences in properties resulted.   The higher aging temperature produced a tensile strength of but 75,000 lb. per sq. in. compared with 109,000 lb. per sq. in. for the alloy aged for 2 hr. at 500° C.   After the subsequent drawing, however, both alloys had the same tensile strength; namely, 140,000 lb. per sq. in.   During the drawing the resistivity of the alloy aged the shorter time decreased while that of the alloy aged for the longer period increased.   These two facts indicate a further precipitation of the nickel-silicon hardener at room temperature brought about by cold work of the alloy of which the properties are illustrated in Fig. 3. Such a precipitation would explain the increased strengthening effect and decrease in resistivity during hard drawing.   This explanation is further strengthened by the fact that hard-drawn wires of this composition showed in some cases considerable increases in strength and change in conductivity when aged at room temperature.

Effect of Low-temperature Aging on Properties of Heat-treated and Hard-drawn Alloys

For the purpose of developing a material with a higher conductivity than was obtained by heat treatment and hard drawing, a study was made of the effect of low-temperature aging on the resistivity and strength of heat-treated and hard-drawn wires.   For this study two representative compositions were chosen; one containing nickel plus silicon, the other cobalt plus silicon.

The results obtained in aging the copper-nickel-silicon alloy No. 2 containing 4 per cent. of nickel plus silicon are shown in Fig. 8.   The rate of aging decreases, as would be expected with the decrease in temperature.   In all cases the effect is appreciable, which indicates that considerable nickel silicide is still in solution in the heat-treated and hard-drawn alloy.

The effect of low-temperature aging on the tensile strength of this alloy is shown in some selected data given in Table 3.

By selecting the proper temperature it is possible to obtain a material with a tensile strength of 140,000 to 150,000 lb. per sq. in. and conductivity of about 40 per cent. of annealed copper.   If the aging is carried out at a higher temperature, higher conductivities are obtained, but at some

sacrifice in tensile strength. It is significant, however, that higher conductivities in relation to tensile strengths were obtained with copper-nickel-silicon alloys than with the heat-treated and hard-drawn copper-cobalt-silicon alloys.
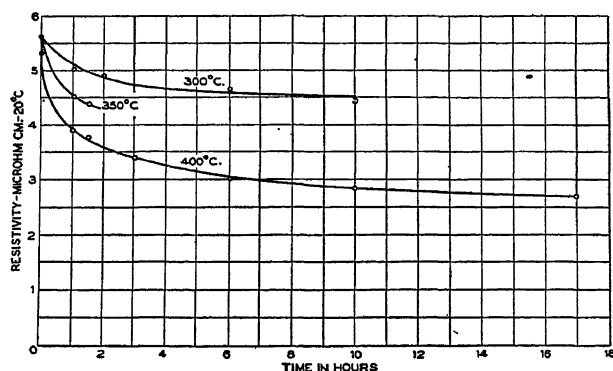
FIG. 8.—EFFECT OF AGING TEMPERATURE ON RESISTIVITY OF HEAT-TREATED AND HARD-DRAWN HARDENABLE COPPER ALLOY CONTAINING 3.1 PER CENT. NI AND 0.75 PER CENT. SI.

The properties obtained in an experimental lot of 1500 ft. of 18 B. & S. gage wire made from alloy 2 in accordance with the process outlined in Fig. 1 are shown in Table 4.

TABLE 3.—*Strength and Resistivity of Heat-treated and Hard-drawn Nickel-silicon-copper Alloy 2 after Aging at Low Temperatures*

Treatment	Ultimate Strength, Lb. per Sq. In.	Resistivity, Microhm Cm. at 20° C.
Hard-drawn..........................	142,000	5.33
Aged 4 hr. 300° C.....................	143,000	4.50
Aged 1½ hr. 350° C..................	139,600	4.35
Aged 1 hr. 400° C.....................	124,000	4.00
Aged 2 hr. 400° C.....................	85,600	3.10

The ultimate strengths in this case are slightly lower than those obtained in the previous studies with short specimens, but may be accounted for by slight changes in the process necessitated in annealing the larger quantities of materials. The elongation of the wire in the finished condition was reduced to 1.5 per cent. when measured over a 60-in. length. This elongation, however, represents sufficient ductility to permit bending about a binding post or at right angles.

The effect on the resistivity of low-temperature aging on a representative copper-cobalt-silicon alloy is shown in Fig. 9.   In this system the resistivity changes are less pronounced than in the case of the copper-nickel-silicon alloys.

TABLE 4.—*Properties of* 18 *B. and S. Gage Wire Made from Alloy* 2
after Treatment Outlined in Fig. 1
ᶜNickel-silicon-copper Wire Containing 4 Per Cent. Nickel Plus Silicon

Coil No.	Diameter, In.	Ultimate Strength, Lb. per Sq. In.	Proportional Limitᵃ Lb. per Sq. In.	Elongation in 60 In., Per Cent.	Resistivity, Microhm Cm. at 20° C.
1	0.040	138,000	94,000	1.5	4.53
2	0.040	138,000	94,000	1.5	4.48
3	0.040	142,000	96,000	1.8	4.49

ᵃ Values obtained from graph drawn on Scott tensile machine.

EFFECT OF STRAIN ON RATE OF AGING OF A QUENCHED NICKEL-SILICON-COPPER ALLOY

Several investigators have observed that mechanical strain accelerates the rate of precipitation of the hardening constituent from a number of solid solutions including lead-antimony[2] and copper-silver[3].   This same behavior was found in a copper-nickel-silicon alloy containing 4 per cent.
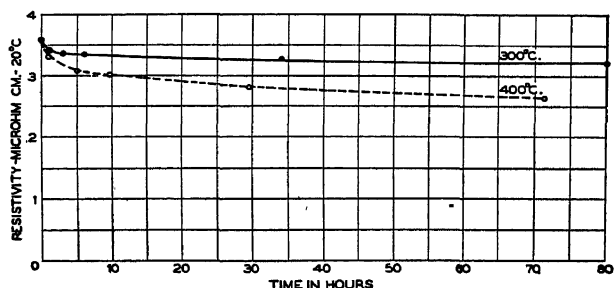
FIG. 9.—EFFECT OF AGING AT TWO TEMPERATURES ON RESISTIVITY OF HEAT-TREATED AND HARD-DRAWN HARDENABLE COPPER ALLOY CONTAINING 2.6 PER CENT. Co AND 0.63 PER CENT. Si.

of nickel plus silicon.   The effect of the aging of quenched, and quenched and hard-drawn wires, at 300°, 400° and 500° C. on the resistivity is shown in Fig. 10.

[2] E. E. Schumacher and G. M. Bouton: The Solid Solubility of Antimony in Lead as Determined by Conductivity Measurements on Cold-worked Alloys. *Jnl.* Amer. Chem. Soc. (1927) **49**, 1667.

[3] A. L. Norbury: Effect of Quenching and Tempering on the Mechanical Properties of Standard Silver.   *Jnl.* Inst. Metals (1928) **39**, 145.

The effect on the tensile strength and resistivity of aging strained wire at 500° C. is shown in Fig. 11. The strain was produced in this case by drawing quenched rod from 0.250-in. dia. to 0.104-in. dia. The unstrained wires were heat-treated in the size 0.104-in. dia. A compari-
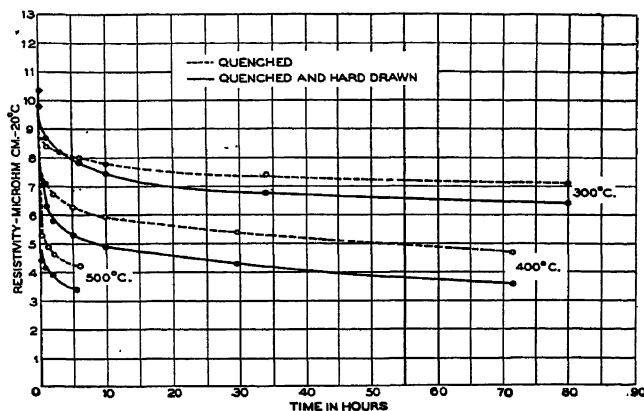
FIG. 10.—ACCELERATION OF PRECIPITATION OF HARDENING CONSTITUENT IN HARDENABLE COPPER ALLOY CONTAINING 3.1 PER CENT. NI AND 0.75 PER CENT. SI, RESULTING FROM MECHANICAL STRAINING OF QUENCHED WIRES. MECHANICAL STRAIN WAS PRODUCED BY HARD-DRAWING WIRE FROM 0.250 TO 0.100-IN. DIAMETER.
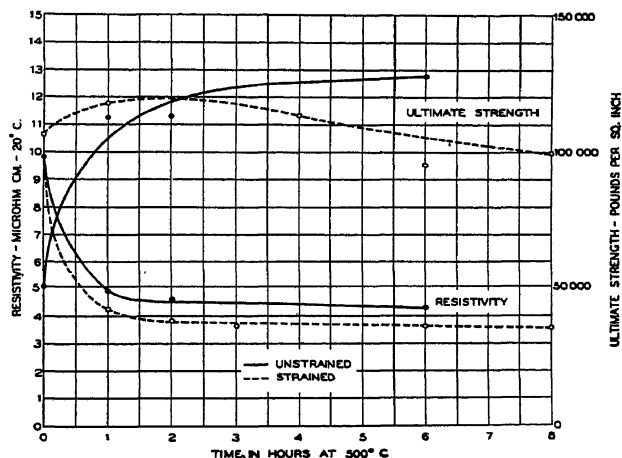
FIG. 11.—EFFECT OF MECHANICAL STRAIN PRIOR TO AGING ON PROPERTIES OF HEAT-TREATED HARDENABLE COPPER ALLOY CONTAINING 3.1 PER CENT. NI AND 0.75 PER CENT. SI. MECHANICAL STRAIN WAS PRODUCED BY HARD-DRAWING WIRE FROM 0.090 TO 0.040-IN. DIAMETER.

son of the tensile curves shows that the strength of the strained material rises to a maximum and then falls off with increase in length of aging time. The unstrained material continued to increase in strength with increase in aging time up to 6 hr. Both the effect on resistivity and on

tensile strength indicate that strain accelerates the rate of precipitation of the hardening constituent.

ACKNOWLEDGMENT

SUMMARY

Hard drawing subsequent to heat treatment materially increased the strength without appreciably increasing the resistivity of copper alloys containing either nickel and silicon or cobalt and silicon. The copper-nickel-silicon alloy containing a nominal 4 per cent. of nickel plus silicon had a maximum strength of 140,000 to 150,000 lb. per sq. in. associated with a conductivity of 30 to 33 per cent. of annealed copper. The copper-cobalt-silicon alloy containing a nominal 1 per cent. of cobalt plus silicon had a strength of 85,000 lb. per sq. in. and a conductivity of approximately 50 per cent. of that of annealed copper. Increasing the amount of hardener to 3 per cent. did not improve the strength or increase the conductivity of this alloy. No improvement in strength resulted from adding cadmium to a copper-nickel-silicon composition.

The aging of heat-treated and hard-drawn wires at temperatures below 500° C. increased the conductivity in alloys containing both nickel and silicon, and cobalt and silicon. The increase was decidedly greater, however, in alloys containing nickel and silicon. If the aging temperature was above 300° C., the tensile strength was adversely affected. The end properties, therefore, depended upon the choice of aging conditions.

It has been shown that strain accelerates the rate of precipitation of nickel and silicon from quenched dispersion-hardening copper-nickel-silicon alloys and determines to some extent the end properties obtained under given aging conditions.

Constituents of Aluminum-iron-silicon Alloys

By William L. Fink* and Kent R. Van Horn,* Cleveland, Ohio

Aluminum forms not only binary compounds with most of the metallic elements but also forms many ternary or more complex constituents. Several of those occurring in the more important alloy systems have been identified under the microscope and the action of various etching reagents has been carefully studied.[1] The determination of the structure and composition of these complex constituents is a matter of some difficulty and little information is available.

X-ray crystal analysis offers a promising method for the study of such constituents. First, and of considerable importance, is the possibility of recognizing the presence of a given constituent by means more positive than microscopic observation. Evidence can also be obtained concerning the nature and composition of the constituent in question and ultimately it should be possible, at least in some cases, to describe the structure including the relative locations of the various atoms.

In this paper some results of an uncompleted study of the constituents of the aluminum-iron-silicon system are given and the methods employed are described. Inasmuch as iron and silicon are the chief impurities in aluminum, the constitutional relations of this system are of fundamental importance in the metallurgy of pure aluminum and its alloys; the system has been studied by several investigators and the more important contributions have been reviewed recently.[2] Fig. 1 shows the structure of the aluminum-rich alloys after prolonged annealing at 560° C., in accord with one of the most recent investigations.[3] The ternary alloys examined in the course of the present investigation were all annealed at 550° or 560° C.; in fact, some of the specimens were the identical ones used by Dix and Heath, who kindly supplied them for this work. Since the results

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[1] See particularly E. H. Dix, Jr. and W. D. Keith: Etching Characteristics of Constituents in Commercial Aluminum Alloys. *Proc.* Amer. Soc. Test. Mats. (1926) **26**, 317.

[2] The Aluminum Industry, **2**, 89. New York, 1930. McGraw-Hill Book Co.

[3] E. H. Dix, Jr. and A. C. Heath, Jr.: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. *Proc.* Inst. of Metals Div., A. I. M. E. (1928) 164.

of this study are consistent, in general, with the observations of Dix and Heath, the nomenclature employed by those investigators and indicated in Fig. 1, will be followed.

PREPARATION OF SPECIMENS

Diffraction patterns were made from specimens prepared by powdering the alloys. Usually these alloys were brittle and could be powdered easily in a steel mortar to pass a 300-mesh screen. The diffraction patterns did not show any lines corresponding to metallic iron, thus
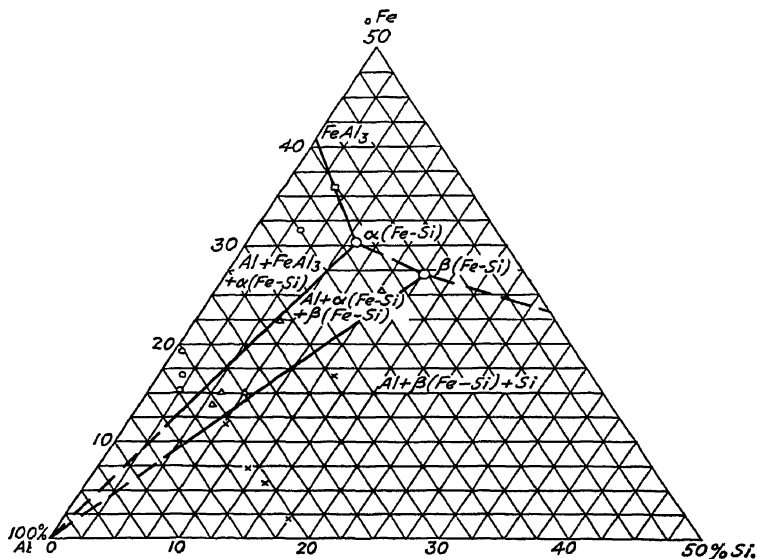
FIG. 1.—ALUMINUM-IRON-SILICON PHASE RELATIONS AT 560° C.   (DIX AND HEATH.)

showing that there was substantially no contamination of the specimens by iron from the mortar.   The powder was placed in one end of a capillary glass tube of about 1 mm. outside diameter.   Sodium chloride was placed in the other end of the tube as a standard.   The alloy specimen was separated from the sodium chloride by a cotton plug, and the capillary tube was sealed at both ends.

In order to obtain more intense reflections it is sometimes desirable to concentrate the constituent or constituents under investigation. Two constituents, FeAl₃ and β(Fe-Si), were obtained in concentrated form as residues from the solution of the alloys in which they occurred. The constituent β(Fe-Si) was prepared by electrolytic separation in a 10 per cent. NaCl solution from an alloy containing 8.40 per cent. iron, 9.44 per cent. silicon and 0.01 per cent. copper as an impurity. This alloy contained free silicon besides β(Fe-Si) and the residue contained

both of these constituents in a much more concentrated form than in the original alloy. A little trouble was experienced from inclusions of hydrated alumina with this residue, although the amount of hydrate was finally reduced by careful swirling and decanting to a point where no alumina lines were shown on the diffraction pattern. $FeAl_3$ was prepared in a similar manner by solution of an alloy made from 99.95 per cent. aluminum and containing 20 per cent. iron. In this case a buffer solution was successfully used to prevent precipitation of alumina.

X-RAY METHODS

Diffraction patterns were made on a General Electric apparatus using a molybdenum target tube operating at 30,000 volts and 20 ma. The exposure periods were 28 to 30 hr. and the specimens were rotated by hand occasionally during this period. In measuring the positions of the lines, corrections were made for any dimensional changes in the films by reference to the sodium chloride standard, which was included with each specimen. The various lines were rated as to intensity, five degrees of intensity being recognized.

SILICON

Good use was made of the X-ray diffraction method in the examination of aluminum-silicon alloys in 1921 in the course of an investigation on the nature of the change produced in these alloys by "modification." It had been suggested that modification was accompanied either by an allotropic change in the silicon or perhaps by the formation of a compound with aluminum. Diffraction patterns of an alloy containing 13 per cent. silicon showed only the lines of elementary silicon and aluminum, regardless of whether the alloy was in the "normal" or "modified" condition. The results showed that modification did not produce any detectable quantity of either an allotropic form of silicon or an aluminum-silicon compound.

In a study of constituents precipitated from supersaturated solid solutions, the diffraction pattern of elementary silicon was obtained on examination of an alloy containing 1.51 per cent. silicon. The specimen had been forged, heated 120 hr. at 570° C., quenched in water and reheated 40 hr. at 400° C. This developed a precipitate visible under the microscope, as shown in Fig. 3. This was the identical specimen previously used in an investigation by Archer, Kempf and Hobbs.[4] It is of interest to note that the lattice parameter was the same as for elementary silicon, indicating, but not definitely proving, that there was little if any aluminum in solid solution in the silicon.

[4] R. S. Archer, L. W. Kempf and D. B. Hobbs: Heat Treatment of Aluminum-silicon Alloys. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 198.

FeAl₃

Binary aluminum-iron alloys up to 40 per cent. iron contain aluminum and a brittle, very hard constituent which Gwyer[5] concluded to be the compound FeAl₃. To confirm the existence of this compound, Dix and Heath prepared an alloy closely corresponding to the theoretical composition. They described the structure as completely homogeneous. Further confirmation of the composition of this constituent has been obtained in the present investigation. Chemical analysis of the residue· obtained from the 20 per cent. iron alloy, as described above, showed an iron content of 41.02 per cent., agreeing closely with the theoretical value of 40.85 per cent. for FeAl₃.
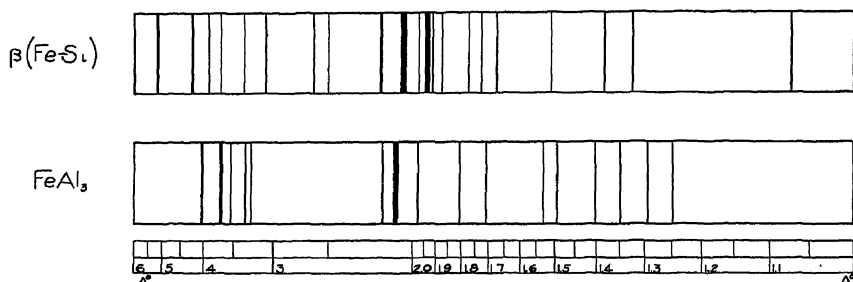
FIG. 2.—INTERPLANAR SPACINGS OF FeAl₃ AND β(Fe-Si).

The interplanar spacings for FeAl₃ determined from pure binary alloys and the separated compound are given in Table 1 and are shown diagrammatically in Fig. 2.

α(Fe-Si)

The diffraction patterns of α(Fe-Si), Table 1, appear almost identical with that of FeAl₃ except for a slight contraction of the lattice, probably a slight change in the axial ratios and some changes in the intensities of the lines, which in some instances caused the disappearance of reflections. This suggests that α(Fe-Si) is a solid solution of silicon in FeAl₃. The change in parameter of FeAl₃ with the addition of silicon is illustrated by the most intense reflection, which shows a variation in interplanar distance from 2.09 Å for FeAl₃ to 2.05 Å for α(Fe-Si). Gwyer and Phillips[6] consider that their metastable β is "most probably a solid solution capable of existence over a wide range of compositions." It is

[5] A. G. C. Gwyer: Alloys of Aluminium with Copper, Iron, Nickel, Cobalt, Lead and Cadmium. *Ztsch. f. anorg. u. allge. Chem.* (1908)·**57, 126.**

[6] A. G. C. Gwyer and H. W. L. Phillips: Constitution of Alloys of Aluminium with Silicon and Iron. *Jnl.* Inst. Metals (1927) **38, 29.**

TABLE 1.—Interplanar Spacings of α(Fe-Si)

Alloys	16.82 Fe, 1.85 Si	15.0 Fe, 2.0 Si	13.84 Fe, 5.65 Si	15.00 Fe, 6.00 Si	22.42 Fe, 6.61 Si	35.91 Fe, 3.95 Si	FeAl₃ (Electrolytic Separation)	FeAl₃ (Determined from 5% and 20% Fe Samples)	Intensities of Reflections α(Fe-Si)	Intensities of Reflections FeAl₃
Treatment of Alloys → Interplanar spacings divided by order of reflection = d/n in Å	2 Weeks at 560° C.	3 Days at 550° C.	2 Weeks at 560° C.	3 Days at 530° C.	5 Weeks at 560° C.	5 Weeks at 560° C.				
	4.00	4.00	4.00	3.99	3.99	4.02	4.01	4.02	Medium	Medium
			3.70		3.70	3.70	3.68	3.68	Medium	Medium
	3.51	3.51			3.51	3.54	3.52	3.52	Weak	Weak +
	3.30	3.30			3.30	3.34	3.31	3.32	Weak	Weak
	3.22	3.21			3.205	3.25	3.25	3.255	Weak	Weak
						3.10	3.08	3.10	Very weak	Very weak
					2.98	2.97	2.51	2.52	Very weak	Very weak
	2.79				2.78	2.775		2.46	Very weak	Very weak
	2.19	2.185	2.18	2.18	2.175	2.18	2.15	2.16	Weak	Weak
	2.125	2.125	2.125	2.12	2.12	2.145	2.08	2.09	Strong	Very strong
	2.07	2.07	2.055	2.05	2.055	2.075	1.975	1.975	Weak	Very weak
					1.97	1.975			Weak	
	1.87	1.88	1.88	1.875	1.865	1.875			Very weak	
	1.78	1.78	1.77	1.77	1.77	1.76	1.798	1.80	Very weak	Very weak
	1.70				1.70	1.70	1.705	1.705	Very weak	Very weak
	1.665		1.67	1.67	1.66	1.66	1.625		Weak	
	1.605	1.60	1.60	1.60	1.60	1.60	1.53	1.536	Weak	Weak
	1.53	1.53			1.53	1.53	1.49	1.495	Very weak	Very weak
	1.479				1.481	1.485	1.395	1.40	Very weak	Weak
	1.40	1.395	1.38	1.382	1.381	1.393	1.339	1.350	Weak	Weak
			1.286	1.286	1.281	1.285	1.285	1.29	Weak	Weak
	1.29	1.29	1.258	1.262	1.261	1.26	1.245	1.252	Weak	Weak
	1.26	1.26			1.250	1.241			Weak	Weak

possible that this constituent is α(Fe-Si), although Gwyer observed no variation in silicon.

The patterns of α(Fe-Si) were all obtained from specimens showing one or more additional constituents; namely, aluminum, $FeAl_3$, or β(Fe-Si). One specimen lay on the binary $FeAl_3$-α(Fe-Si) line of Fig. 1, and showed only a faint reflection of the strongest line of the aluminum pattern. The other lines were those of α(Fe-Si) and $FeAl_3$ superimposed. The lines of α(Fe-Si) were found in all specimens examined in which Dix and Heath had observed this constituent under the microscope, as indicated in Fig. 1, and were not found in any of the specimens examined in which the constituent had not been observed.

Although the diffraction results indicate that α(Fe-Si) is a solid solution of silicon in $FeAl_3$, there is information which does not seem to be entirely consistent with this conclusion. Microscopic examination of alloys containing α(Fe-Si) showed a sharp line of demarcation between the α(Fe-Si) sheath and the remainder of the $FeAl_3$ needle from which it was derived (Fig. 4). A gradual transition might be expected if α(Fe-Si) is a solid solution with variable composition. However, it would be possible to explain the sharp transition if the rate of diffusion of silicon in α(Fe-Si) is very rapid in comparison to the rate in $FeAl_3$. The fact that equilibrium has not been attained in high-iron alloys treated at 560° C. for five weeks indicates a very slow diffusion velocity of the silicon atoms in $FeAl_3$. More information concerning the exact nature of α(Fe-Si) could be obtained by even longer annealing treatments. If α(Fe-Si) is a true solid solution, $FeAl_3$ would not be present in ternary alloys under equilibrium conditions at 560° C.

It is possible that the sharp division between solid solutions and intermetallic compounds is arbitrary and does not accurately represent the natural differentiation. There may be a group of constituents which have some of the characteristics of both solid solutions and compounds. It is conceivable, for example, that a constituent might be susceptible to discontinuous variations in composition. If α(Fe-Si) were such a constituent, the observed X-ray and microscopic data would be consistent.

β(Fe-Si)

The constituent β(Fe-Si) gave an X-ray pattern entirely different from those of the other constituents in the system. The diffraction measurements are recorded in Table 2. The interplanar spacings for β(Fe-Si) determined from specimens containing about 80 per cent. aluminum, 7 to 15 per cent. iron and 5 to 11 per cent. silicon are the same regardless of the phase field in which the alloy occurred; they are diagrammatically represented in Fig. 2. The identical spacings would indicate either a definite compound or a constituent in which the param-
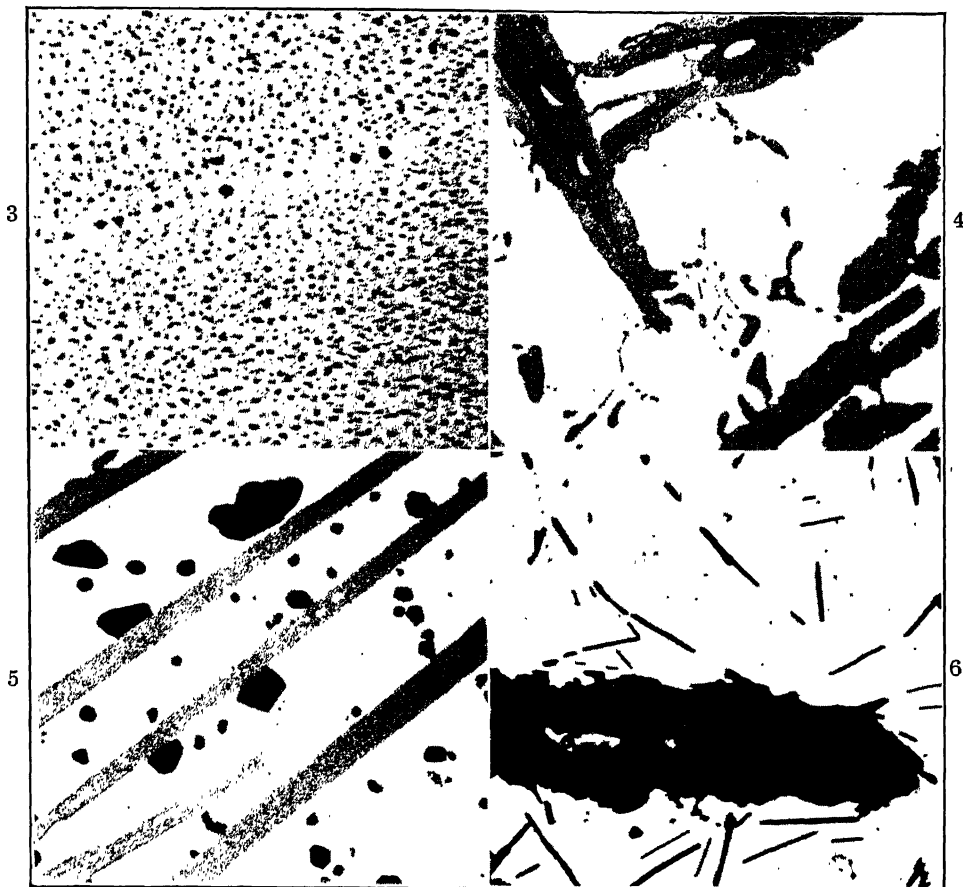
Fig. 3.—Reprecipitated silicon in 1.51 per cent. silicon alloy.   × 500
(Archer, Kempf and Hobbs.)

Forged, heated 120 hr. at 570° C.; quenched, and reheated 40 hr. at 400° C.
Etched in 1 per cent. HF.

Fig. 4.—Chill-cast aluminum-iron-silicon alloy containing 16.82 per cent.
iron and 1.85 per cent. silicon.   × 500.   (Dix and Heath.)

Annealed for two weeks at 560° C. and quenched.   Etched 40 sec. with 25 per
cent. HNO_3 at 70° C.   Shows aluminum matrix α(Fe-Si) and $FeAl_3$.   Cores of
particles are $FeAl_3$ in relief.

Fig. 5.—Chill-cast aluminum-iron-silicon alloy containing 7.29 per cent.
iron and 11.77 per cent. silicon.   × 500.   (Dix and Heath.)

Annealed two weeks at 560° C. and quenched.   Shows aluminum matrix, silicon
(dark) and needles of β(Fe-Si).   Unetched.

Fig. 6.—Chill-cast aluminum-iron-silicon alloy containing 13.84 per cent.
iron and 5.65 per cent. silicon.   × 500.   (Dix and Heath.)

Annealed two weeks at 560° C. and quenched.   Etched 20 sec. with 0.5 per cent.
HF.   Shows aluminum matrix, β(Fe-Si) dark, and a core of α(Fe-Si).

eters are a function of the aluminum content. An alloy containing considerably less aluminum should eliminate one of the possibilities.

The X-ray pattern of an alloy containing 61.4 per cent. aluminum, 25.2 per cent. iron and 13.4 per cent. silicon consisted entirely of β(Fe-Si) lines (Table 2). Microscopic examination revealed the presence of particles of a constituent (probably aluminum solid solution) in such quantities that X-ray reflections would not be expected. The interplanar spacings were appreciably smaller than those obtained from the samples described above. It would seem, therefore, that β(Fe-Si) is a ternary compound which may have an excess of aluminum in solid solution, which causes an expansion of the lattice.

The diffraction evidence confirms the previous microscopic examination of alloys containing the constituent β(Fe-Si). The appearance of β(Fe-Si) in each of the phase fields in which it occurs is represented in Figs. 5 and 6.

The authors intend to continue the investigation of the aluminum-iron-silicon system with particular reference to the crystal structure of the stable ternary constituents.

TABLE 2.—*Interplanar Spacings of β(Fe-Si)*

Alloys	7.29 Fe 11.77 Si	8.0 Fe 10.0 Si	13.84 Fe 5.65 Si	15.0 Fe 6.0 Si	8.0 Fe 10.0 Si	25.2 Fe 13.36 Si	Intensities of Reflections
Treatment of Alloys	2 Weeks at 560° C.	3 Days at 550° C.	2 Weeks at 560° C.	3 Days at 550° C.	Electrolytic Separation of β(Fe-Si)	3 Days at 600° C. 1 Day at 580° C. 3 Days at 560° C.	
Interplanar spacings divided by order of reflection = $\frac{d}{n}$ in Å.	5.20		5.20		5.20	5.17	Medium
	4.25	4.25	4.25	4.23	4.25	4.21	Medium
	3.90	3.90			3.90		Very weak
	3.69		3.70			3.66	Very weak
	3.44		3.43			3.41	Very weak
			3.08	3.07		3.07	Weak
	2.617	2.62	2.61	2.61		2.60	Weak
	2.50		2.52			2.49	Very weak
						2.29	Weak
	2.17	2.17	2.18	2.18	2.18	2.17	Medium
	2.025	2.03	2.025	2.02	2.025	2.03	Strong
	1.975					1.975	Very weak
	1.935	1.93	1.94	1.94	1.925	1.93	Strong
	1.87	1.87	1.87	1.875	1.875	1.87	Weak
	1.765	1.77	1.77	1.77	1.77	1.76	Very weak
	1.72	1.72	1.72			1.713	Weak
	1.67	1.67	1.67	1.67	1.67	1.662	Weak
	1.51		1.50			1.495	Very weak
	1.378	1.376	1.38	1.382	1.382	1.375	Weak
	1.324		1.329	1.328	1.330	1.32	Weak
	1.07	1.071	1.075	1.076	1.075	1.07	Weak

DISCUSSION

(H. W. Gillett presiding)

F. KELLER, New Kensington, Pa.—This paper is interesting to us because it corroborates the work done by Dix and Heath on the aluminum-iron-silicon system and because it shows that we have not reached the limit to which we may go with the microscope.

We do not agree with Dr. Fink that it is easier to determine the presence of new constituents by this method, especially when they occur in small amounts. We admit that he can determine the nature of these constituents better than we can, but we think that we can find them with less trouble.

On page 388 it is stated that the α(Fe-Si) apparently is a solid solution of silicon in $FeAl_3$, but that the microscopic examination did not seem to substantiate this. In Fig. 4 the line of demarcation shown between the particles of $FeAl_3$ and the α(Fe-Si) may be a result of polishing and etching. Solid solutions and compounds do show such characteristics when they are polished and etched. It is possible that the diffusion of silicon is extremely slow; in fact, we are led to believe that it is. If we obtain equilibrium conditions by longer heating, it is possible that there would be no $FeAl_3$. Determining whether or not this is possible would again be done better by the microscope than by the X-ray, at least we can see when it happens.

H. W. GILLETT, Columbus, Ohio.—Many people have struggled with these iron-aluminum-silicon compounds, and they have been pretty much of a mystery. Certainly anything that elucidates them is of great fundamental value.

R. S. ARCHER, Cleveland, Ohio.—The statement in the paper regarding the possibilities of the diffraction method is that by this method a given constituent can be recognized more *positively* by microscopic methods. I think we agree with Mr. Keller that, in many cases at least, the diffraction method may be less sensitive than the microscopic method. The big value of it is that recognition may be more positive. There is a definite test for a crystalline entity, whereas in microscopic work we frequently have to depend on etching effects, color, hardness and other characteristics which are not so definite.

It is perhaps unnecessary to call attention to the important part that this method is now playing in the study of alloy constitution. An excellent illustration was afforded in Mr. Sykes' discussion of the tungsten-carbon system, in which he used this method to identify the carbides of tungsten.[7]

W. L. FINK.—In regard to the question of the microscopic or the diffraction method of identifying constituents, Fig. 2 is interesting. Sometimes in the microscopic examinations of small particles, it is very difficult to distinguish slight differences in color, whereas the difference between the corresponding diffraction patterns can be seen easily. In Fig. 2 the top pattern is that of the β (Fe-Si) and the lower that of $FeAl_3$. You see there is a tremendous difference. You do not have to make measurements to see the difference.

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[7] See page 227.

Of course, if the constituents are present in small amounts, it is generally impossible to obtain enough lines to serve the purpose. However, by using the method described in the paper for separating or concentrating the constituent, a very good pattern can usually be obtained.

E. H. DIX, JR., New Kensington, Pa.—We do not want to start an argument regarding metallography or microscopy on the one hand and the X-ray on the other. I am sure we all feel that both tools are extremely valuable. It was with a great deal of gratification that I learned from Fink and Van Horn that their X-ray data checked very closely with our microscopic results. I must admit that I felt much better about the system. Nevertheless, I do want to say one thing for the microscope. I want to ask Dr. Fink if he will reply to this question. Assuming that you did not have a general diagram of these constituents and that you were not looking for a difference between FeAl₃ and α(Fe-Si), is there sufficient difference between the patterns you have obtained to lead you to believe that there were two separate constituents? What I have in mind is this: microscopically we sometimes have trouble separating constituents which exhibit only slight differences in etching characteristics; in this case there were apparently only very slight differences in the spacing in the X-ray pattern. Were those differences great enough to make you certain that there were two constituents?

W. L. FINK.—If we had had a very limited number of samples, it might not have been apparent that we had two constituents, without careful measurements, but for those samples in which the two constituents occur together, there is a distinct broadening of the lines. In any case, I believe careful measurement would have revealed the difference. There was a greater difference between FeAl₃ and α(Fe-Si) than there was between the patterns from the pure beta, and beta that existed in the presence of excess aluminum. In the latter instance we do not conclude that there is a separate constituent. Perhaps if we had been working on this system without a knowledge of previous work and without microscopic examination, we would not have given a separate name to α(Fe-Si), but might have said that we had FeAl₃ and FeAl₃ in which silicon was dissolved. That is, the nomenclature might have been different.

A. G. C. GWYER AND H. W. L. PHILLIPS, Warrington, Lancs., England (written discussion).—This paper is an interesting example of the use of X-rays for identifying microconstituents in alloys and it is to be hoped that the authors will be able to follow it up by single-crystal work and so determine the lattices of certain of the more important constituents of this alloy system. The authors have been successful in developing a method of extracting FeAl₃ and β(Fe-Si) from alloys containing these constituents, and it should not prove unduly difficult, by selecting an appropriate composition, and adopting an extremely slow rate of solidification, to obtain isolated crystals sufficiently large not only for Laue work but also for crystallographic measurement. The isolation of α(Fe-Si) would appear to be more difficult, since in our experience it is impossible to select a composition in which the whole of the iron is present as this constituent. Any chemical method of separation must therefore be capable of differentiating between FeAl₃ and α(Fe-Si) or between α(Fe-Si) and β(Fe-Si). The problem is a difficult one but perhaps not insuperable, and we should be interested to learn whether Messrs. Fink and Van Horn have met with any success in this direction.

We were interested to see that the authors had been able to obtain a diffraction pattern of silicon reprecipitated from solid solution in aluminum, and that they had been able to detect no difference between the lattice parameter of reprecipitated and elementary silicon. We are not familiar with the apparatus used by the authors, and

it is to be regretted that the paper contains no information regarding its sensitivity. According to Gayler and Preston,[8] who used precision methods of measurement, and copper radiation, the lattice parameter of pure aluminum is 4.041 Å while that of aluminum saturated with silicon at 513° C. is 4.039 Å. Had a molybdenum anode and the ordinary powder method been used, diffraction images corresponding with the (111) planes would have been obtained at 17° 24′ 16″ (pure Al) and 17° 24′ 48″ (solid solution). We should be interested to know whether such small differences could have been detected with the apparatus used by Fink and Van Horn. If not, it seems that even such a guarded conclusion as that the apparent identity of the parameters of reprecipitated and elementary silicon indicates little or no solid solubility is hardly justified.

$FeAl_3$ is one of the few constituents of this system that can be examined in an uncontaminated state, and its diffraction spectrum therefore should be obtainable with a high degree of reliability. It is stated by Groth[9] to crystallize in the monoclinic system, having constants

$$a:b:c = 1.5413 : 1 : 1.9158$$
$$\beta = 107° 41'.$$

So far as we know, no figures have been published regarding the density of $FeAl_3$, but from some experiments carried out in this laboratory it is of the order of 3.84 grams per cubic centimeter. We have attempted to reconcile these data with the diffraction spectrum given in the present paper by calculating the interplanar spacings, plotting them logarithmically and superposing, and it would appear that a reasonably good agreement is obtained on the assumption that the lattice parameter is 4.4 Å and that the unit cell contains three molecules of $FeAl_3$, the first observed image being due to (002). There are many lines missing from the observed spectrum but we have not attempted to theorize on the arrangement of the atoms within the unit cell or to calculate the possible interferences.

As the authors state, it is impossible to isolate the constituent α(Fe-Si) and one is tempted to wonder whether sufficient care has been taken in compiling Table 1 to discriminate between lines due to α(Fe-Si) and those due to other constituents, and here the publication of spectrographs would have been very helpful. For example, an alloy containing 35.91 per cent. Fe and 3.95 per cent. Si would contain $FeAl_3$ and α(Fe-Si). Do the authors wish to convey that its spectrum contains lines at 4.02, 3.70, 3.54, 3.34 . . . . Å due to α(Fe-Si) together with others at 4.02, 3.68, 3.52, 3.32 . . . Å due to $FeAl_3$? It seems inconceivable. Of the alloys detailed in Table 1, Nos. 3 and 4 (13.84 Fe:5.65 Si and 15.00 Fe: 6.00 Si) lie well within the field of Al — α(Fe-Si) — β(Fe-Si) phase of Fig. 1, and we see no reason to dispute the authors' view that these particular alloys are free from $FeAl_3$. Their spectra are free from a large number of the lines present in $FeAl_3$, and on the other hand, they contain lines at 2.18, 1.88, 1.67, 1.26 Å which are common to all the alloys (1 to 6) but which do not occur in $FeAl_3$. We are inclined to think that the authors attach too much weight to the alloy containing 22.42 per cent. Fe, 6.61 per cent. Si (No. 5 in the table). According to Fig. 1, it lies just within the Al — α(Fe-Si) — β(Fe-Si) field and very close to the boundary between this field and that of Al — $FeAl_3$ — α(Fe-Si). We rather question whether the alloy is, in fact, entirely free from $FeAl_3$. As cast, it would contain a large proportion of this constituent, and we question whether an annealing period of five weeks at 560° would be adequate to ensure its disappearance. Can it be that the lines at 3.51, 3.30, 3.205, 1.70 etc., are evidence of the

[8] M. L. V. Gayler and G. D. Preston: The Age-hardening of Some Aluminum. Alloys. *Jnl.* Inst. Metals (1929) 41, 191.

[9] P. H. Groth: Chemische Krystallographie, I. Leipzig, 1906. W. Englemann.

presence of FeAl₃? However this may be, it is clearly legitimate to state that the spectrum of α(Fe-Si) contains certain lines in positions nearly identical with some of those of the FeAl₃ spectrum, but it must not be overlooked that it contains certain lines from which the FeAl₃ spectrum is free. We do not consider, therefore, that the authors are justified, on the published evidence, in stating that the α(Fe-Si) spectrum as a whole is almost identical with that of FeAl₃, nor do we think that the deduction that α(Fe-Si) is a solid solution of Si in FeAl₃ is a legitimate one. They attempt to reconcile the sharp line of demarcation between FeAl₃ and α(Fe-Si) in their micro-sections with this theory by suggesting a novel concept regarding solid solutions; namely, that they may be susceptible to discontinuous variations in composition. Do they maintain that this theory can be reconciled with the facts regarding α(Fe-Si) which have been established by methods of thermal analysis? Had they, or Dix and Heath before them, taken cooling curves, they would have found, as we did,[10] that α(Fe-Si) was the product of a peritectic reaction between FeAl₃ and liquid, marked by a well defined arrest. It displays all the characteristics, thermal and microscopic, of an individual constituent.

We should have been interested to see the analysis of the β(Fe-Si) extracted electrolytically from an alloy, and are somewhat surprised to find that electrolytic separation was not employed in a greater number of instances, particularly so as the most characteristic β(Fe-Si) lines are missing from the spectrum of the sample separated in this manner. The authors state that β(Fe-Si) is a ternary compound which may have an excess of aluminum in solid solution. It is impossible to reconcile this with the fact that we were able to show a photomicrograph of silicon reprecipitated from its supersaturated solid solution in β(Fe-Si).

W. L. Fink and K. R. Van Horn (written discussion).—The consideration of a possible crystal structure of FeAl₃ derived from our measurements, suggested by Messrs. Gwyer and Phillips, is a valuable contribution. The absence of a number of reflections can be explained by the short exposures, the interferences caused by the atomic arrangement, and the intentional omission of lines 2.02 Å and 1.436 Å on account of the coincidence with aluminum reflections.

The X-ray methods used for lattice parameter measurements could not reveal the minute angular variations mentioned in the discussion on reprecipitated silicon. However, the diffraction results have been subsequently supplemented by chemical analysis of the precipitated silicon particles. Generally samples of separated constituent are examined under the microscope and any particles with adhering aluminum or other material are discarded. In this case the state of subdivision of the precipitate approached colloidal dimensions and a mechanical separation was impossible. Analysis showed that the total aluminum (dissolved and adhering) was 0.7 per cent. The chemical results also indicate that there is little if any solubility of aluminum in silicon.

It was pointed out in the article and the oral discussion that the reflections of α(Fe-Si) and FeAl₃ overlap, resulting in broader lines when the two constituents are simultaneously present. The position of each component reflection was estimated by measuring to the corresponding edge of the line. In other words, there are two sets of reflections, one for FeAl₃ and the other for α(Fe-Si), as shown in Table 1.

It was stated in the paper that there were "changes in the intensities of the lines which in some instances caused the disappearance of reflections." Some doubt was expressed in the written discussion concerning this explanation. The diffraction results published in the paper were obtained from films exposed 28 to 30 hr. Additional patterns have been made with 72 hr. exposures from the samples listed in col-

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[10] A. G. C. Gwyer and H. W. L. Phillips: Reference of footnote 6.

umns 1, 3, 5, 6 in Table 1.   A number of reflections missing in the original films were present after prolonged exposures.   The pattern of the alloy containing 16.82 per cent. Fe and 1.85 per cent. Si revealed reflections corresponding to 3.70, 3.09, 2.52, 1.97, 1.35 and 1.25 Å.   The additional lines obtained in the pattern of the 13.84 per cent. Fe, 5.65 per cent. Si alloy corresponded to 3.51, 3.30, 3.20 and 1.335 Å.   A 48-hr. exposure of a binary 40 per cent. iron alloy revealed additional reflections at 2.805, 1.88, 1.66, 1.62, 1.261 Å.   These supplementary X-ray data show that the absence of reflections was due to variation in intensity rather than to the presence of a phase with a fundamentally different lattice.   The resemblance between the patterns of α(Fe-Si) and FeAl$_3$ is now more apparent and it would seem that the suggestion that α(Fe-Si) is a solid solution of silicon in FeAl$_3$ is the most plausible explanation of the results.

Two possible explanations for the line of demarcation between the constituents α(Fe-Si) and FeAl$_3$ observed in the microstructure were presented in the paper. Gwyer and Phillips question whether one of these explanations could be reconciled with the thermal results.   It would appear that this conception is more consistent with the thermal data than the hypothesis of two phases with a distinctly different crystal structure is with the X-ray measurements.   However, the authors do not consider that this is necessarily the most probable interpretation.   Mr. Keller proposed a likely explanation.

Assuming that α(Fe-Si) and the β of Gwyer and Phillips are identical, the constituent would be formed with the evolution of heat.   However, a thermal arrest is not necessarily accompanied by a crystallographic transformation.   The A$_2$ point in iron is the classic illustration.   In the aluminum-titanium system[11] a pronounced thermal point was observed at about 665°C.   No alteration in the crystal structure of the TiAl$_3$ constituent could be detected.   The literature indicates that the aluminum-manganese system may exhibit similar thermal characteristics.

The X-ray results have shown no indication of solution of silicon in β(Fe-Si) in the range investigated.   The photomicrograph of the alloy containing 4.0 Fe and 17.0 per cent. silicon published by Gwyer and Phillips[12] is interpreted by them in terms of such solubility.   The observed structure could be explained by the simultaneous precipitation of β(Fe-Si) and silicon during eutectic solidification.   It would seem improbable that the silicon present could be dissolved in the β(Fe-Si) by heat treatment.

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[11] W. L. Fink, K. R. Van Horn and P. M. Budge.   See page 421.
[12] *Loc. cit.*

Equilibrium Relations in Aluminum-antimony Alloys of High Purity

By E. H. Dix, Jr.,* F. Keller† and L. A. Willey,† New Kensington, Pa.

The consideration of alloying elements for aluminum has led to a series of investigations of the equilibrium relations between aluminum and those alloying elements. Therefore, the aluminum end of the aluminum-antimony diagram has been studied.

The general form of the aluminum-antimony equilibrium diagram has been worked out by Campbell and Mathews[1] and by Tammann.[2] Campbell and Mathews described principally the beginning of solidification. They found the curve of beginning of solidification rising gradually from the melting point of pure aluminum to a maximum at about 67 per cent. aluminum. After a slight lowering of the curve at a little greater antimony concentration the curve again rises to a maximum at 18.4 per cent. aluminum, which corresponds to the compound AlSb. The curve then drops to the melting point of pure antimony. Tammann explained the maximum occurring at about 67 per cent. aluminum as the result of the slow formation of the single compound AlSb.

The space lattice of the compound AlSb, according to Owen and Preston,[3] is face-centered cubic, the antimony atoms being intermeshed with an identical aluminum lattice.

Very little, if any, work has been done on aluminum alloys containing small amounts of antimony.

The Present Investigation

It has been the purpose of this investigation to determine the solid solubility of antimony in aluminum and also to investigate the eutectic temperature and concentration. The experimental work has been carried out in a manner similar to that described in a previous paper[4] from this laboratory.

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[1] W. Campbell and J. A. Mathews: The Alloys of Aluminum. *Jnl.* Amer. Chem. Soc. (1902) **24**, 258.

[2] G. Tammann: Uber Aluminum Antimonlegierungen. *Ztsch. f. anorg. Chem.* (1906) **48**, 53.

[3] E. A. Owen and G. D. Preston: Atomic Structure. *Jnl.* Inst. Metals (1925) **34**, 480.

[4] E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans.* A. I. M. E. (1926) **73**, 560.

Electrolytically refined aluminum of high purity was used.[5] An analysis showed the following composition: Cu, 0.008 per cent.; Si, 0.019; Fe, 0.010; Ti, 0.001; Al (by difference), 99.962 per cent.

The antimony was obtained in the form of lumps and contained the following impurities: Si, 0.01 per cent.; Fe, 0.01; Zn, 0.01; As, 0.10; Sb (by difference), 99.86 per cent. A hardener containing 13 per cent. antimony was prepared from the materials and used to make up the alloys for this investigation.

Preparation of Alloys

The alloys were prepared by melting the aluminum in an Acheson graphite crucible and then adding the required amount of antimony hardener. The melting was done in a small Hoskins electric crucible furnace. Previous to pouring, the melt was thoroughly stirred and skimmed. For solubility determination, bars ½ by ⅝ by 9 in. were cast in an open horizontal iron mold. A sample for chemical analysis was cast from each melt in the form of a ⅛-in. plate. The chemical analyses were made on drillings from the cast plates. The chemical analyses and the method of casting the alloys are given in Table 1.

TABLE 1.—*Aluminum-antimony Alloys*

Alloy No.	Analysis			Method of Casting
	Silicon, Per Cent.	Iron, Per Cent.	Antimony, Per Cent.	
4964	0.01	0.01	0.10	Chill-cast in iron mold.
4965	0.01	0.01	0.21	
4966	0.02	0.01	0.36	
4967	0.02	0.01	0.46	
4968	0.02	0.01	1.02	
4969	0.02	0.01	3.16	
5264			1.04	Cast in hot graphite mold.
5269			1.14	

Methods of Heat Treatment

Specimens of a convenient size for microscopic examination were cut from the chill-cast bars of the alloys. Sets of these alloys were heated at various temperatures for a sufficient length of time to produce equilibrium and then quenched. The maximum temperature used was 645° C. and the minimum was 200° C. The specimens heated at 200° C. were first heated at 540° C. for one week and quenched. They were then reheated at 200° C. in a salt bath for 7½ weeks. A complete list of the heat treatments is given in Table 2.

[5] F. C. Frary: Electrolytic Refining of Aluminum. *Trans.* Amer. Electro-Chem. Soc. (1925) **47**, 275.

FIGS. 1–6.—CAPTIONS ON OPPOSITE PAGE.

TABLE 2.—*Heat Treatment of Aluminum-antimony Alloys*

Group 1.

  M 4964 to 4969 inclusive,
  168¾ hr. at 540° C. and quenched.

Group 2.

  M 4964 to 4969 inclusive,
  244 hr. at 500° C. and quenched.
  244 hr. at 500° C., cooled to 450° C. in 43 hr., held 385 hr. and quenched.
  244 hr. at 500° C., cooled to 400° C. in 499½ hr., held 146½ hr. and quenched.
  244 hr. at 500° C., cooled to 350° C. in 884½ hr., held 208½ hr. and quenched.
  244 hr. at 500° C., cooled to 300° C. in 1308½ hr., held 368 hr. and quenched.

Group 3.

  M 4964 to 4969 inclusive,
  119½ hr. at 645° C. and quenched.

Reheating.

  M 4964 to 4969 inclusive,
  168¾ hr. at 540° C., and quenched,
  reheated at 200° C. for 1246 hr. and quenched.

Microstructure of the Alloys

The solid solubility of antimony in aluminum appears to be less than 0.10 per cent. The microscopic examination of the chill-cast alloy containing 0.10 per cent. antimony showed very small particles of the AlSb constituent. Subsequent to the various solution heat treatments, examination showed this alloy to have particles of the AlSb constituent out of solution.

The small particles of constituent forming a somewhat discontinuous network in a chill-cast alloy are shown in Figs. 1 and 2. The alloy contained 0.46 per cent. antimony. Fig. 3 shows the structure of another chill-cast alloy that contained 1.02 per cent. antimony and Fig. 4 shows the structure after solution heat treatment at 540° C. A distinctly hypereutectic structure in a chill-cast alloy containing 3.16 per cent. antimony is shown in Figs. 5 and 6.

FIG. 1.—0.46 PER CENT. SB ALLOY CHILL-CAST IN IRON MOLD. × 100.
Etched with 0.5 per cent. HF. Shows primary aluminum areas and eutectic network of aluminum and aluminum-rich AlSb constituent.
FIG. 2.—0.46 PER CENT. SB ALLOY CHILL-CAST IN IRON MOLD. × 500.
Etched with 0.5 per cent. HF. Shows eutectic network in greater detail.
FIG. 3.—1.02 PER CENT. SB ALLOY CHILL-CAST IN IRON MOLD. × 100.
Etched with 0.5 per cent. HF. Shows eutectic structure with large areas of primary aluminum.
FIG. 4.—1.02 PER CENT. SB ALLOY ANNEALED 168 HR. AT 540° C. AND QUENCHED. × 100.
Etched with 0.5 per cent. HF. Shows small particles of AlSb constituent after the above treatment.
FIG. 5.—3.16 PER CENT. SB ALLOY CHILL-CAST IN IRON MOLD. × 100.
Etched with 0.5 per cent. HF. Shows the hypereutectic structure of this alloy
FIG. 6.—3.16 PER CENT. SB ALLOY CHILL-CAST IN IRON MOLD. × 500.
Etched with 0.5 per cent. HF. Shows the form of the primary AlSb constituent.

FIGS. 7–9.—CAPTIONS ON OPPOSITE PAGE.

Eutectic Concentration and Temperature

The examination of an alloy containing 1.04 per cent. antimony that had been slowly cooled through the freezing range in a hot graphite mold showed this alloy to be hypoeutectic. The microstructure of the alloy is shown in Figs. 7 and 8.
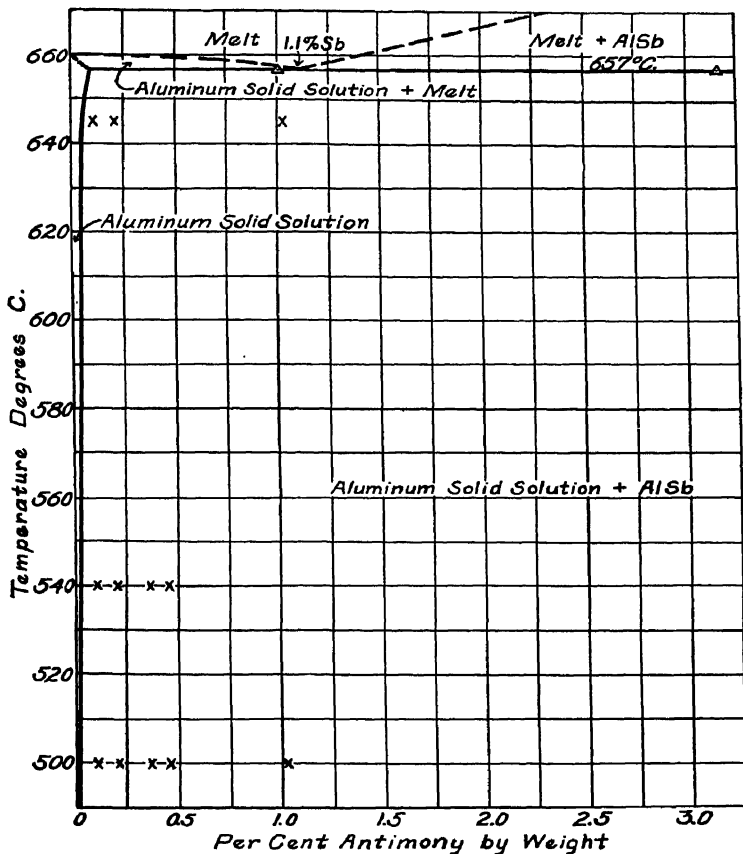
FIG. 10.—ALUMINUM END OF ALUMINUM-ANTIMONY DIAGRAM.

FIG. 7.—1.04 PER CENT. SB ALLOY SLOWLY COOLED THROUGH FREEZING RANGE IN HOT GRAPHITE MOLD.   × 100.
Etched with 0.5 per cent. HF.   Shows a hypoeutectic structure.
FIG. 8.—1.04 PER CENT. SB ALLOY SLOWLY COOLED THROUGH FREEZING RANGE IN HOT GRAPHITE MOLD.   × 500.
Etched with 0.5 per cent. HF.   Shows platelike form of constituent frequently occurring in aluminum-antimony alloys of approximately eutectic concentration.
FIG. 9.—1.14 PER CENT. SB ALLOY SLOWLY COOLED THROUGH FREEZING RANGE IN HOT GRAPHITE MOLD.   × 100.
Etched with 0.5 per cent. HF.   Shows a few particles of primary AlSb constituent in a slightly hypereutectic alloy.

Although this alloy did not show a true eutectic structure, a similar alloy of slightly higher concentration, 1.14 per cent. antimony, showed a few particles of primary constituent, probably AlSb.   It was apparently impossible to produce a uniform eutectic structure, as both primary aluminum and primary aluminum-antimony compound occurred in the same field, as is shown in Fig. 9.

Cooling curves were taken on two of the alloys, containing 1.02 and 3.16 per cent. antimony, in determining the eutectic temperature. Two hundred grams of metal were melted down in a small Hoskins crucible furnace employing a closed graphite crucible as a container. The furnace was controlled so as to permit a cooling rate of 6° to 8° per minute.   The temperatures were taken with a platinum, platinum-rhodium thermocouple in connection with a Leeds & Northrup precision potentiometer.   The couple was protected from molten aluminum by following the practice recommended by the Bureau of Standards.[6]   The results obtained from the cooling curves indicated a eutectic temperature of 657° C.

Aluminum End of Aluminum-antimony Diagram

Fig. 10 shows the solubility relations at the aluminum end of the aluminum-antimony system as determined by this investigation.   The solid solubility is less than 0.10 per cent. at temperatures as high as 645° C.   The eutectic concentration lies at about 1.1 per cent. antimony and the eutectic temperature at 657° C.

ACKNOWLEDGMENT

The authors desire to acknowledge with thanks the preliminary work of Mr. A. C. Heath, Jr. on this investigation and to express appreciation to Mr. H. V. Churchill, under whose direction the chemical analyses were made.

DISCUSSION

(H. W. Gillett presiding)

H. W. GILLETT, Columbus, Ohio.—It is interesting to have this flow of papers on fundamentals of the aluminum systems from the laboratories of the Aluminum Co. of America.   At this rate of progress, it will not be long before we will be obliged to have a second, enlarged edition of that wonderful book, "The Aluminum Industry," than which there is no better on any metallurgical subject.[7]

I noted a statement that Mr. Dix made in presenting the papers, that this aluminum-antimony proposition was purely academic.   I do not believe that statement would pass in some European circles without considerable comment.   It would be

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[6] U. S. Bur. Stds. *Tech. Paper* 170 (1921) 193.

[7] J. D. Edwards, F. C. Frary and Z. Jeffries: The Aluminum Industry.   New York, 1930.   McGraw-Hill Book Co.

interesting if someone could give us a little authoritative information on the status of these antimony alloys, the type of K-S Seewasser.

F. KELLER, New Kensington, Pa.—We have had a number of samples of the K-S Seewasser in this country, and we found antimony in them.

Some information not contained in this paper shows that in order to introduce antimony into aluminum it is necessary to use a fairly high temperature. For instance in some of the alloys, we have to go 200° or 300° C. above the temperature we would normally use. While they work without difficulty we do not see the advantage of going to the extra effort to put it in, because the results do not seem to show that we gain much advantage.

R. S. ARCHER, Cleveland, Ohio.—The Seewasser alloy is a German development, largely due, I believe, to Dr. Sterner-Rainer. It seems to contain about 3 per cent. manganese, about 0.75 per cent. antimony and some 2 or 3 per cent. of magnesium. It is recommended especially for resistance to salt-water corrosion. According to reports from Germany, it seems to be good in that respect. Most of the work is concerned with sand castings. The tensile properties of this alloy in the sand-cast condition are comparable with those of the 8 per cent. copper alloy, No. 12. Its casting properties are difficult. Because of the high manganese content, the alloy is sluggish and requires high pouring temperatures. Also, it is more apt to form dross than are the more common aluminum alloys. We have noticed a recent change in the recommended composition, to include about 0.9 per cent of silicon, which is said to decrease the casting difficulties.

There is little use of the alloy in this country. What its status is abroad we scarcely know by first-hand information.

E. H. DIX, JR.—I still maintain that the binary aluminum-antimony system, as far as we can see, is academic.

The analyses which have been made on foreign samples of the K- S Seewasser alloy have indicated a large variation in antimony content, which is probably caused by the tendency toward pronounced segregation, which Mr. Keller mentioned. The alloy itself, that is, the aluminum-manganese-magnesium alloy, without the antimony, has very excellent corrosion resistance, and would therefore show much better corrosion results than, say, the aluminum-copper alloys.

It is claimed, I believe, that the value of antimony consists in the type of film that is formed because of the presence of the antimony in the alloy. This may or may not be substantiated in later experience.

Equilibrium Relations in Aluminum-magnesium Silicide Alloys of High Purity

E. H. Dix, Jr.,* F. Keller† and R. W. Graham,† New Kensington, Pa.

ALUMINUM alloys containing relatively small amounts of magnesium and silicon are of commercial interest because they are readily workable in the annealed form and may be hardened and strengthened by suitable heat treatment. An intermediate temper can be produced in these alloys by quenching after a solution heat treatment and the alloy in this condition can be formed easily. Artificial aging is required to obtain the maximum mechanical properties but this aging does not cause distortion nor require elaborate heat-treating equipment.

The hardening of the alloys after quenching is attributable in part to the retention of the compound Mg₂Si in solid solution, while the maximum hardness obtained by subsequent artificial aging is attributed to the fact that the solid solubility of the compound Mg₂Si in aluminum decreases with decreasing temperature.

Considering the importance of aluminum alloys susceptible to heat treatment, it is surprising how few fundamental investigations have been carried out on the aluminum-magnesium silicide alloys.

This paper deals principally with the solid solubility relations of the compound Mg₂Si in aluminum and is the sixth paper of a series[1] from the laboratories of the Aluminum Co. of America reporting the results of investigations of equilibrium relations in aluminum-base alloys made from high-purity aluminum.[2]

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[1] E. H. Dix, Jr.: Note on the Microstructure of Aluminum-Iron Alloys of High Purity. *Proc.* Amer. Soc. Test. Mat. (1925) **25**, Pt. 2, 120.

E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans.* A. I. M. E. (1926) **73**, 560.

E. H. Dix, Jr. and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 315.

E. H. Dix, Jr. and A. C. Heath, Jr.: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 164.

E. H. Dix, Jr. and F. Keller: Equilibrium Relations in Aluminum-magnesium Alloys of High Purity. *Trans.* A. I. M. E., Inst. Met. Div. (1929) 351.

[2] F. C. Frary: Electrolytic Refining of Aluminum. *Trans.* Amer. Electro-Chem. Soc. (1925) **47**, 275.

PREVIOUS INVESTIGATIONS

Hanson and Gayler[3] made an extensive investigation of the constitution of aluminum alloys containing various amounts of magnesium and silicon. A part of the investigation consisted in determining the solid solubility of the compound Mg_2Si in aluminum. As a result of their
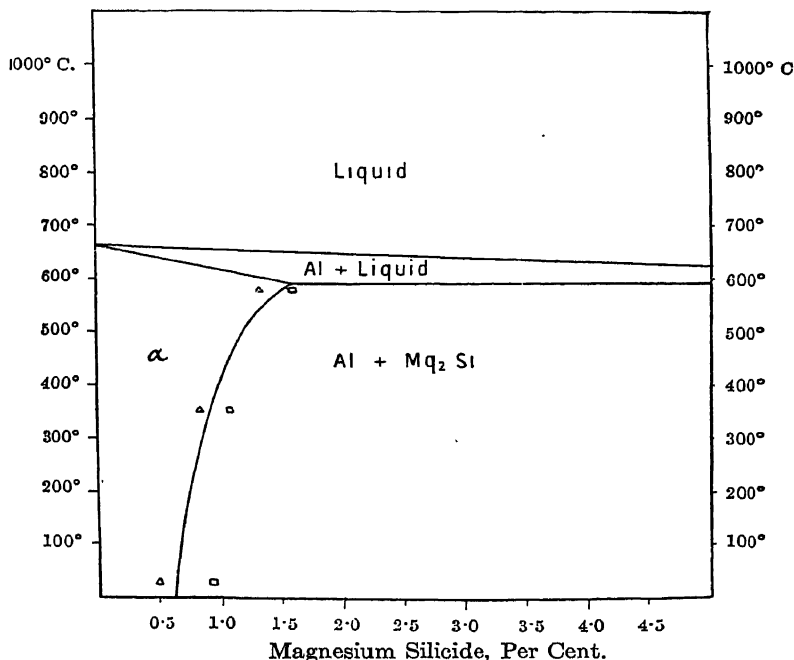
FIG. 1.—SOLID SOLUBILITY CURVE ACCORDING TO HANSON AND GAYLER.

work the diagram shown in Fig. 1 was published. This indicates that 1.6 per cent. of the compound Mg_2Si is soluble in aluminum at the eutectic temperature, and that the solubility decreases with decreasing temperature until at 30° C. it is less than 0.6 per cent.

THE PRESENT INVESTIGATION

In previous investigations made in these laboratories it has been the practice to make solubility determinations on chill-cast samples annealed for long periods to establish equilibrium. Since the alloys used in the present investigation were readily workable, the solubility determinations

[3] D. Hanson and M. L. V. Gayler: Constitution and Age-Hardening of the Alloys of Aluminum with Magnesium and Silicon. *Jnl.* Inst. Met. (1921) **26,** 321.

Eleventh Report to Alloys Research Committee on Some Alloys of Aluminum. Inst. Mech. Engrs. (1921) 234.

were made on sheet specimens.   By using this type of specimen equilibrium conditions could be obtained with much shorter heating periods, because in the wrought form the cast network is broken up and diffusion takes place more readily.
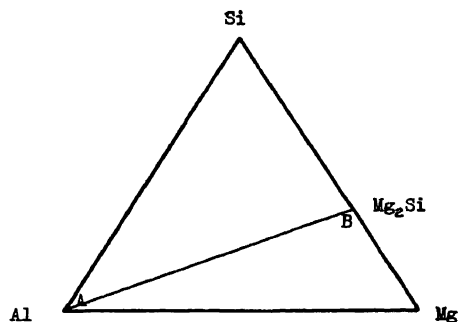
FIG.   2.—ALUMINUM-MAGNESIUM-SILICON DIAGRAM.

In the system of aluminum, magnesium and silicon, all alloys lying on a base line running from the aluminum corner, A in Fig. 2, of a triangle representing the ternary alloys to the point B representing the composition of the compound Mg_2Si on the binary line Mg-Si form a simple eutectiferous series.   The alloys used for this investigation were calculated to contain magnesium and silicon in the proper ratio to form the compound and may be considered as binary alloys.[4]

Materials for Investigation

High-purity aluminum similar to that employed in the previous investigations was used.   The analyses of this and other metals used for the alloys are given in Table 1.

TABLE 1.—*Analyses of Metals Used in Investigation*

Metal	Silicon, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Manganese, Per Cent.	Titanium, Per Cent.	Aluminum, Per Cent.	Magnesium, Per Cent.
Aluminum.....	0.007	0.009	0.016	Nil	0.002	99.966	
Silicon.........	98.64	0.66	Nil	0.04	0.10	0.56	
Magnesium[a]...	Nil	Nil				0.01	99.98

[a] The magnesium contained 0.01 per cent. of other Group II metals.

For the preparation of the alloys of this series a hardener containing approximately 15 per cent. silicon was first made up by adding metallic silicon to molten aluminum at a temperature of about 1400° F.   This hardener was remelted and sufficient magnesium was added to form 20 per cent. of magnesium silicide, by introducing the solid magnesium under the surface of the molten alloy

A series of alloys of varying magnesium silicide content was then prepared by adding the requisite amount of this hardener to high-purity aluminum.   The metal was melted in a plumbago crucible in a coke-

[4] W. Guertler: Considerations in Theoretical Metallurgy.   *Metall und Erz* (1920) **17**, 192.

fired furnace, for which the coke was carefully dried. Sheet ingots 7 by 8 by 1½ in., weighing approximately 8 lb., were cast in a tilting iron mold. Small ingots for thermal analysis and ⅛ in. thick chill-cast plate samples for chemical analysis were prepared at the same time.

Chemical Analyses

Chemical analyses obtained from the plate samples are given in Table 2.

TABLE 2.—*Chemical Analyses of Cast Plate Samples*

Mark	Desired Composition Mg$_2$Si, Per Cent.	Analysis Mg, Per Cent.	Si, Per Cent.	Calculated from Analysis Mg$_2$Si, Per Cent.	Excess Constituent Mg, Per Cent.
4677	0.15	0.11	0.05	0.14	0.03
4678	0.30	0.20	0.10	0.27	0.03
4741	0.45	0.31	0.17	0.46	0.02
4680	0.55	0.41	0.20	0.55	0.07
4681	0.75	0.43	0.23	0.63	0.03
4682	1.00	0.67	0.36	0.98	0.05
4683	1.25	0.82	0.46	1.25	0.03
4684	1.50	0.98	0.55	1.50	0.03
4685	1.75	1.16	0.62	1.69	0.09
4839	1.80	1.18	0.65	1.77	0.06
4742	2.00	1.21	0.76	2.07	0.00
4840	2.25	1.58	0.87	2.37	0.08

TABLE 3.—*Chemical Composition of Sheet Specimens*

Mark	After Annealing for Solubility Determinations Mg, Per Cent.	Si, Per Cent.	Mg$_2$Si Calculated from Analysis, Per Cent.	Excess Constituent, Per Cent.	After Heat Treatment for Mechanical Property Tests Mg, Per Cent.	Si, Per Cent.	Mg$_2$Si Calculated from Analysis, Per Cent.	Excess Constituent, Per Cent.
4683	0.79	0.45	1.23	0.01 Mg				
4684	0.98	0.52	1.42	0.08 Mg				
4685	1.16	0.61	1.67	0.10 Mg				
4830	1.15	0.59	1.61	0.13 Mg	1.18	0.60	1.64	0.14 Mg
4742	1.27	0.65	1.77	0.15 Mg	1.32	0.66	1.80	0.18 Mg
4840	1.33	0.77	2.10	0.00	1.47	0.77	2.10	0.14 Mg

Some segregation in the sheet ingot was anticipated and for this reason the magnesium silicide content of the sheet samples used for the solid-solubility determinations was checked. Samples for chemical analysis were prepared from sections of the sheet that had been annealed and examined microscopically. The results of the analyses obtained in this

manner are given in Table 3.   It was feared that the long annealing treatment might cause some difference in composition through distillation of magnesium from the specimens.   However, the results in Table 3 indicate that the composition of the specimens was the same after the long-time heating for the solubility determination as after a heat treatment of 15 min. in the nitrate bath.

Thermal Analysis

The results of cooling curves taken on several of the alloys to locate the liquidus line are given in Table 4.   For this work the small ingots previously referred to, each weighing 200 grams, were melted in a graphite crucible in a small electric furnace and the melt cooled at the rate of 2° per minute.   Temperature readings were taken on a Leeds & Northrup potentiometer in conjunction with a platinum, platinum–rhodium thermocouple.   The practice recommended by the Bureau of Standards[5] for protecting the couple in molten aluminum was followed.

The temperature of the eutectic arrest was determined by taking a cooling curve on a 200-g. sample of an alloy of approximately the eutectic composition (13 per cent. Mg_2Si).   The results obtained are in agreement with those of Hanson and Gayler.   The eutectic arrest occurs at 595° C.

TABLE 4.—*Results of Thermal Analysis to Determine Liquidus*

Mark	Mg_2Si, Per Cent.	Temperature of Initial Thermal Arrest on Cooling, Deg. C.
4641	.46	655
4682	.98	651
4684	1.50	646
4840	2.37	645

Fabrication of Sheet

The ingots previously described were hot-rolled from 1.5 in. to 0.25 in.   The resulting slab was annealed and slowly cooled in the furnace. The slab was then cold-rolled to 0.125 in., annealed, and finally cold-rolled to 0.064 in.   The finished sheet was slightly blistered, the degree of severity apparently increasing directly with the percentage of the Mg_2Si compound.

Tensile test specimens and samples for metallographic examination were cut from this sheet.

Annealing Treatments

The apparatus and methods used for heating to establish equilibrium have been described in detail in several of the publications from these laboratories and therefore will not be described here.

[5] U. S. Bur. Stds. *Tech. Paper* 170 (1921) 193.

Specimens from the as-rolled 0.064-in. sheet were heated for various periods of time at 570° C. and quenched. An examination of the structure indicated that no further change was produced by increasing the annealing period from 48 to 72 hr. It was felt, therefore, that 72 hr. could be safely used to produce equilibrium conditions at this high temperature.

For the determination of the solubility relations at the lower temperatures, the specimens after being heated 72 hr. at 570° C. were slowly cooled to the desired temperature, held at that temperature long enough to establish equilibrium conditions, then quenched. For studying the solubility relations at 300° C. and 200° C. respectively, it was desired to approach equilibrium from two directions; hence, in addition to cooling to the desired temperature in the manner described, specimens previously quenched from equilibrium at 570° C. were subsequently reheated at 300° and 200° C. and quenched. A summary of the various heat treatments is given in Table 5.

The sheets after heating were severely blistered and the higher concentrations presented a blackened appearance, probably the result of slight decomposition at the surface.

TABLE 5.—*Heat Treatment of Aluminum-magnesium Silicide Alloys*

A. SOLUBILITY DETERMINATION

First Group

Contained specimens marked 4677, 4678, 4741, 4680, 4681, 4682, 4683, 4684, 4685, 4742

Heated 72 hr. at 570° C. and quenched.

Heated 72 hr. at 570° C., cooled to 500° C. in 24 hr., held 24 hr., and quenched.

Heated 72 hr. at 570° C., cooled to 400° C. in 72 hr., held 24 hr., and quenched.

Heated 72 hr. at 570° C., cooled to 300° C. in 120 hr., held 24 hr., and quenched.

Heated 72 hr. at 570° C., cooled to 200° C. in 192 hr., held 24 hr., and quenched.

Second Group

Specimens marked 4685, 4839, 4742, 4840 heated 72 hr. at 580° C. and quenched.

Reheating

Specimens marked 4677, 4678, 4741, 4680, 4681, 4682, 4683, 4684, 4685, 4742.

Heated 72 hr. at 570° C. and quenched. Reheated five weeks at 200°C. in salt bath and quenched.

Specimens marked 4742, 4685, 4684, 4683.

Heated 72 hr. at 570° C. and quenched. Reheated 24 hr. at 300° C. and quenched.

B. SOLIDUS DETERMINATION

Specimens marked 4677, 4678, 4741, 4680, 4681, 4682, 4683, 4685, 4839, 4742, 4840.

Heated 24 hr. at 580° C., raised to 600° C. in ½ hr., held 15 min. and quenched.

Heated 24 hr. at 580° C., raised to 610° C. in 1 hr., held 15 min. and quenched.

Heated 24 hr. at 580° C., raised to 628° C. in 1½ hr., held 15 min. and quenched.

C. HEAT TREATMENT FOR MECHANICAL PROPERTIES

Specimens marked 4677, 4678, 4741, 4680, 4881, 4682, 4683, 4684, 4685, 4839, 4782, 4840.

Heat-treated 15 min. at 500° C. in fused nitrate bath and quenched.

Heat-treated 15 min. at 530° C. in fused nitrate bath and quenched.

Heat-treated 15 min. at 560° C. in fused nitrate bath and quenched.

Heat-treated 15 min. at 560° C. in fused nitrate bath and quenched, and aged 18 hr. at 160° C.
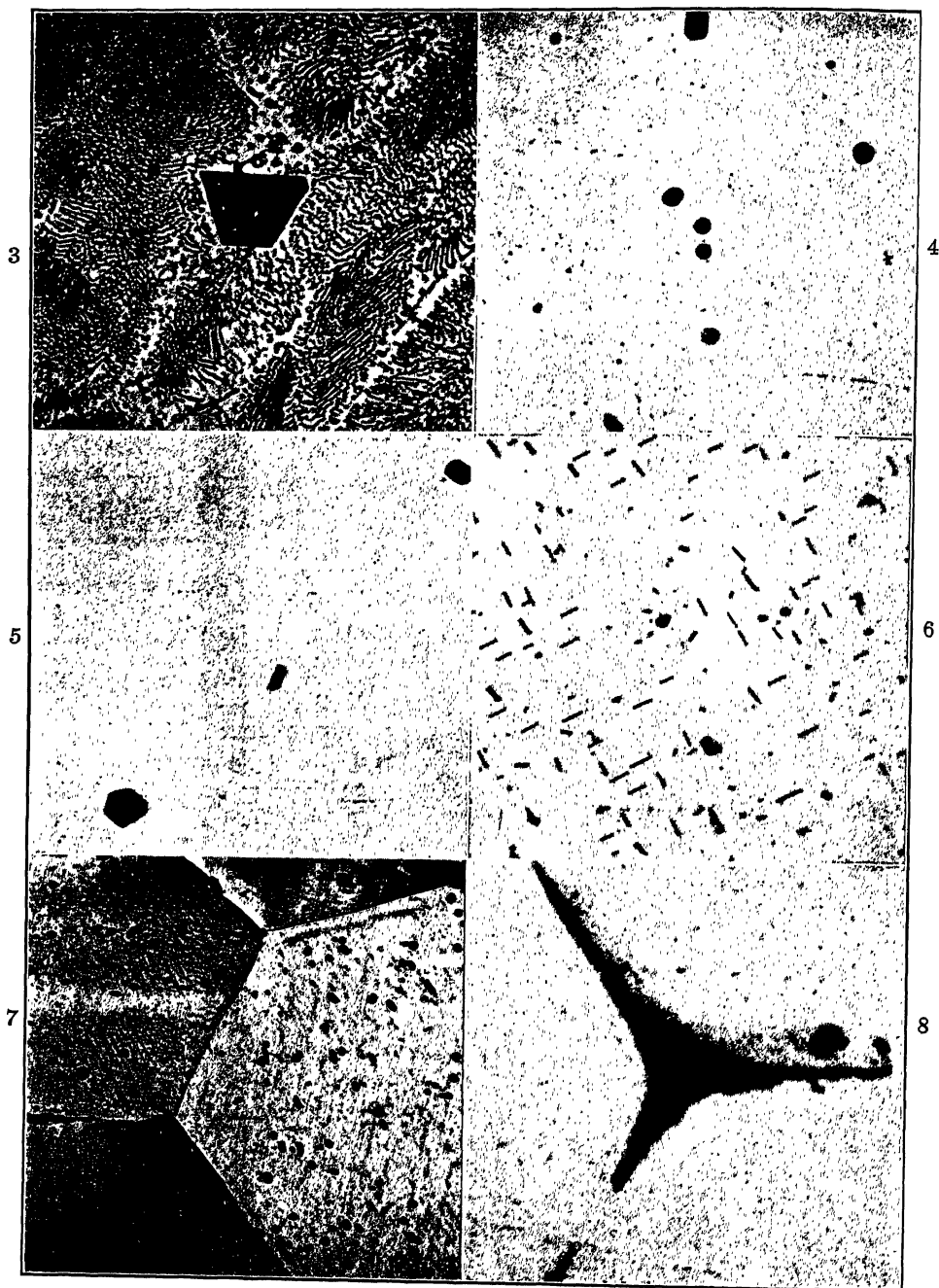
FIGS. 3–8.—CAPTIONS ON OPPOSITE PAGE.

Microscopic Examination

Composite specimens, of a convenient size, $\frac{1}{2}$ by $\frac{3}{4}$ in. in section by $\frac{1}{2}$ in. high, suitable for polishing for microscopic examination, were made up by clamping six pieces of sheet between two heavier mounting sheets in such a manner that in each sheet the surface at right angles to the direction of rolling was prepared for polishing. This surface was first cut plane on a large Jung microtome and then ground on wet broadcloth pads, first with 60C alundum and finally with heavy magnesium oxide in the usual manner.

Each of the composite specimens represented six different Mg_2Si contents quenched from equilibrium at a single temperature. By placing these sections in the composite specimen in order of their concentration, it was possible to locate the solubility limits at one temperature by the examination of the one composite specimen. The specimens in general were not etched, as all the etching reagents known for aluminum alloys attacked the compound Mg_2Si and removed its characteristic deep blue color. For revealing very fine particles and removing surface flow it was found advisable to etch some of the specimens by swabbing with a 0.5 per cent. solution of hydrofluoric acid in water.

When correctly polished the compound Mg_2Si appears pale blue in color but readily tarnishes to a deep iridescent blue. The compound is readily attacked by water in the polishing operation and this consequently makes the preparation of specimens somewhat difficult.

The microstructure of an alloy of approximately eutectic composition (13 per cent. Mg_2Si) is shown in Fig. 3. A large crystal of primary Mg_2Si may be noted surrounded by the aluminum-magnesium silicide eutectic. The tendency toward definite geometrical shape shown by the particle is characteristic of the occurrence of this constituent.

FIG. 3.—ALUMINUM ALLOY M6053 (13 PER CENT. Mg_2Si). × 500.
Chill-cast in graphite mold, etched with 0.5 per cent. HF. Shows primary particles of Mg_2Si in matrix of aluminum-Mg_2Si eutectic.

FIG. 4.—ALUMINUM ALLOY M4742 (1.77 PER CENT. Mg_2Si). × 500.
Heated 72 hr. at 570° C. and quenched. Unetched. Shows small particles of Mg_2Si remaining after treatment.

FIG. 5.—ALUMINUM ALLOY M4683 (1.23 PER CENT. Mg_2Si). × 500.
Heated 72 hr. at 570° C., slowly cooled to 500° C., held 24 hr. and quenched. Unetched. Shows small particles of Mg_2Si remaining after treatment.

FIG. 6.—ALUMINUM ALLOY M4742 (1.77 PER CENT. Mg_2Si). × 500.
Heated 72 hr. at 570° C. and quenched. Reheated 24 hr. at 300° C. and quenched. Unetched. Shows coalesced particles of Mg_2Si resulting from reheating.

FIG. 7.—ALUMINUM ALLOY M4682 (0.98 PER CENT. Mg_2Si). × 100.
Heated 72 hr. at 570° C., slowly cooled to 500° C., held 24 hr. and quenched. Etched with 5 per cent. HF + 10 per cent. HNO_3. Boundaries of solid solution grains have been revealed by etching. Dark areas in matrix are either etching pits or result of oxidation.

FIG. 8.—ALUMINUM ALLOY M4685 (1.67 PER CENT. Mg_2Si). × 2000.
Heated slowly to 600° C. and quenched. Unetched. Shows area at junction of grains where incipient fusion had occurred.

In Fig. 4 particles of Mg_2Si are shown in an alloy containing 1.77 per cent. Mg_2Si quenched from equilibrium at 570° C. This alloy represented the lowest concentration that showed excess Mg_2Si after the above treatment.

In Fig. 5 particles of Mg_2Si are shown in an alloy containing 1.23 per cent. Mg_2Si after it had been annealed 72 hr. at 570° C., slowly cooled to 500° C., held 24 hr. and quenched. This alloy represented the lowest concentration of Mg_2Si that showed excess constituent when quenched from equilibrium at 500° C.

The structural condition produced by reheating an alloy containing 1.77 per cent. Mg_2Si at 300° C. after it had been quenched from equilibrium at 570° C. is shown in Fig. 6. The arrangement of the particles indicated that precipitation had occurred on the octahedral planes.

The reheating, for five weeks at 200° C., of a series of alloys containing from 0.14 to 2.10 per cent. Mg_2Si previously quenched from equilibrium at 570° C., failed to cause the Mg_2Si particles to coalesce to a size that could be seen under the microscope. However, reheating, for 24 hr. at 300° C., specimens previously quenched from equilibrium at higher temperatures, resulted in the development of particles that could be recognized readily.

Fig. 7 illustrates the structure of an alloy containing 0.98 per cent. Mg_2Si which had been annealed 72 hr. at 570° C., slowly cooled to 500° C., held 24 hr. and quenched. The grain boundaries are clearly revealed but the etching reagent has attacked the solid solution matrix, as shown by the severe pitting.

Solubility Curve

A modified solubility curve based on the results of microscopic examination of a series of alloys of varying Mg_2Si content quenched from equilibrium at five different temperatures is shown in Fig. 9.

The liquidus line was drawn from results obtained by taking cooling curves on four alloys to locate the temperature of primary separation. The solidus line was located by heating alloys of the various concentrations above the eutectic temperature and examining for evidence of melting. The first evidence of solid solution melting appeared as cavities at the junctions of several grains, as illustrated in Fig. 8. Alloys in which considerable melting had occurred showed rounded cavities at regular intervals along the grain boundaries. Alloys containing more than 1.23 per cent. Mg_2Si showed indications of severe melting when heated to 600° C.

The maximum solubility at the eutectic temperature as determined by this investigation was 1.85 per cent. of the compound Mg_2Si. This is about 0.2 per cent. higher than the maximum solubility given by Hanson and Gayler. However, the point used by them to limit the solubility

at 580° C. was described as being doubtful.   From 1.85 per cent. Mg_2Si
at the eutectic temperature the solubility decreases rapidly to less than
0.27 per cent. at 200° C.   The value at 200 °C. is considerably lower than
reported by other investigators.   The saturation limits for magnesium
silicide in aluminum are given in Table 6.   The values obtained from the
curve of Hanson and Gayler are also included, for comparison.

TABLE 6.—*Temperature Solubility Relations*

Temperature, deg. C.............	595	500	400	300	200
Saturation limit Mg_2Si, per cent...	1.85	1.05	0.53	0.30	0.27
Saturation limit (Hanson and Gayler)......................	1.60	1.15	.95	.80	.70

Mechanical Properties of Heat-treated Alloys

The solubility curve of Fig. 9 shows a difference of about 1.6 per cent.
Mg_2Si between the maximum solubility at the eutectic temperature and
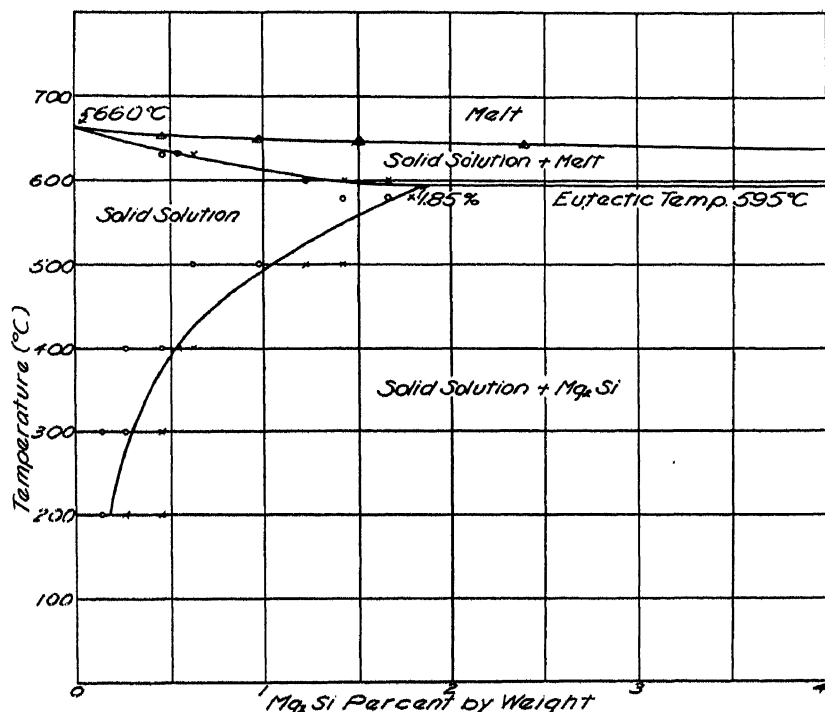
FIG. 9.—MODIFIED SOLUBILITY CURVE.

at room temperature.   The increase in mechanical properties after heat
treatment in the intermediate temper (as quenched) is a result of the

retention of Mg₂Si in solid solution. Heat treatment of the alloys consists of heating just below the solidus for a sufficient length of time to cause solution of the Mg₂Si and quenching to retain this compound in solid solution.
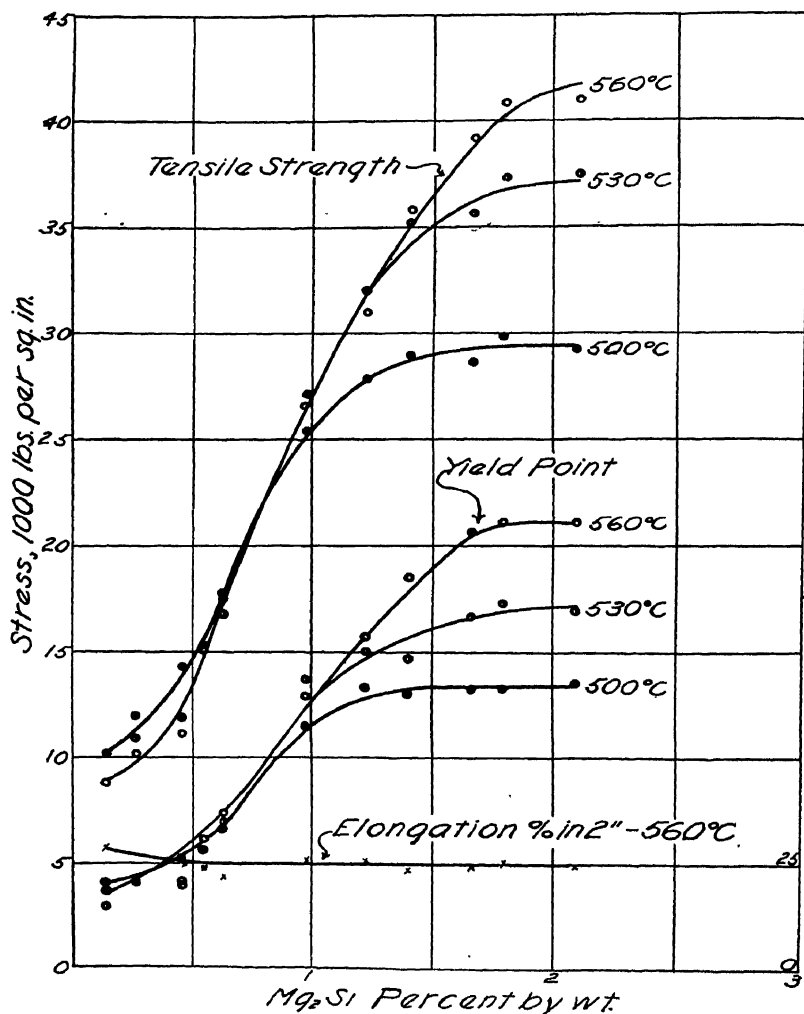
FIG. 10.—MECHANICAL PROPERTIES OF ALUMINUM-MAGNESIUM SILICIDE ALLOY SHEET AFTER QUENCHING.

Immediately after quenching the alloys are easily worked or formed but gradually become harder and stronger in the course of a few months as a result of the precipitation of finely dispersed particles of Mg₂Si from the metastable supersaturated solid solution.

The alloys at this time have experienced an increase in strength and hardness (not elongation) but not the maximum obtainable.   To produce this maximum, it is necessary to age at a slightly elevated temperature to cause further precipitation and coalescence of the finely dispersed particles
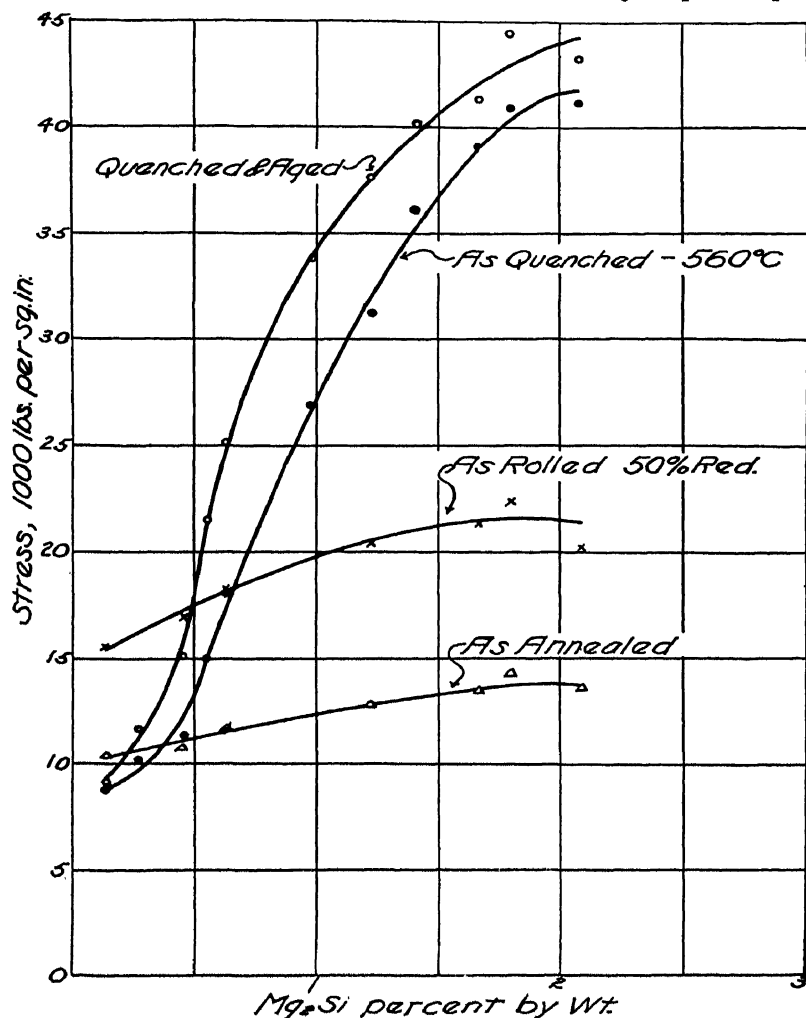
FIG. 11.—COMPARISON OF TENSILE PROPERTIES OF HARD-ROLLED, ANNEALED, HEAT-TREATED, AND HEAT-TREATED AND ARTIFICIALLY AGED ALUMINUM-MAGNESIUM SILICIDE ALLOY SHEET (14 GAGE, 0.064 IN.).

to a critical size, in which condition they exert the maximum interference to slip.

In order to obtain the effect of variations in magnesium silicide content on the mechanical properties, tensile test specimens from the entire series

of alloys used in the solubility determinations were heat-treated for 15 min. in a fused nitrate bath at 500°, 530° and 560° C. respectively.   These specimens were tested one week after heat treatment, and probably a small amount of age-hardening had taken place during that time.   The results of the mechanical tests are shown in Fig. 10.   The tensile strength and yield point increase with increasing magnesium silicide content until the saturation limit is reached for the heat-treating temperature used. The elongation values obtained for alloys containing from 0.14 to 1.0 per cent. Mg_2Si were not consistent, but in general decreased from 27 to 25 per cent.   The values for alloys containing more than 1 per cent. were more consistent, showing a constant elongation of 25 per cent.

The effect of artificial aging was determined on all of the alloys in the series.   Tensile test specimens were heat-treated for 15 min. at 560° C. in a fused nitrate bath and subsequently aged 18 hr. at 160° C.   The tensile properties of annealed, hard-rolled, heat-treated, and heat-treated and aged 14-gage sheet (0.064 in.) are shown by the curves in Fig. 11.

The hard-rolled specimens received a 50 per cent. final reduction in thickness by cold-working.   The annealed material was produced by heating the hard-rolled material for 16 hr. at 345° C. and slowly cooling in the furnace.   The heat-treating and aging procedure is described in Table 4.

The curves in Fig. 11 show that the annealed alloy containing 0.14 per cent. Mg_2Si has a slightly higher tensile strength than the same alloy after heat treating or heat treating and aging.   The annealed material in this instance was very fine grained, while the heat-treated material was very coarse grained.   The coarse grain structure of the heat-treated specimens probably accounts for the low tensile strength exhibited by these specimens.

The effect of artificial aging is most pronounced in alloys containing from 0.6 to 1.0 per cent. Mg_2Si and it is suggested that in this range the aging treatment had caused coalescence of Mg_2Si sufficient to produce critical dispersion.

The elongation values after aging varied from 24 per cent. for the alloy containing 0.14 per cent. Mg_2Si to 15 per cent. for the alloy containing 2.10 per cent. Mg_2Si.

DISCUSSION

(H. W. Gillett presiding)

R. S. ARCHER AND L. W. KEMPF, Cleveland, Ohio (written discussion).—Since the hardening of aluminum alloys by heat treatment depends on solution and precipi-

tation effects, the importance of having accurate curves of solid solubility for the chief hardening additions is obvious.

Inasmuch as the authors have included some discussion of mechanical properties, additional data may be of interest. Age-hardening tests have been made on an alloy containing 1.05 per cent. magnesium and 0.55 per cent. silicon, representing a magnesium silicide content of 1.49 and an excess of 0.11 per cent. magnesium. This alloy was prepared from electrolytically refined ingot of about 99.95 per cent. purity and showed on analysis 0.04 per cent. iron and 0.03 per cent. copper. The alloy was cast in the form of ingots 3½ in. square and hot-forged to approximately 1-in. square bars. These were heated 72 hr. at 590° C. and quenched in water at room temperature. About ⅛ in. of metal was milled from the outside of the bars in preparing flat surfaces for Brinell hardness tests. The hardness tests were made immediately after quenching and after various periods of aging at room temperature, at 150° C.
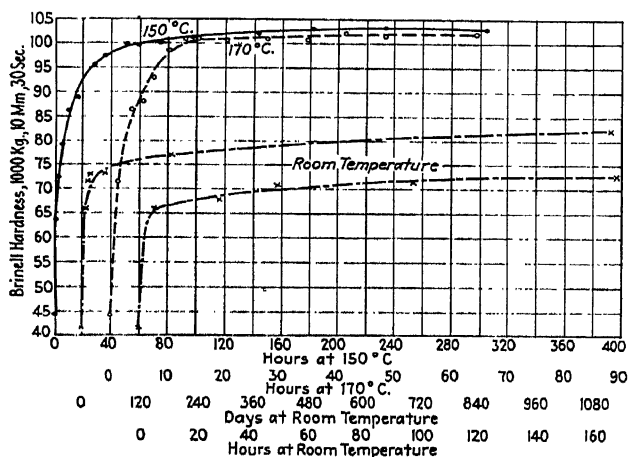
FIG. 12.—PRECIPITATION HARDENING OF WROUGHT ALLOY CONTAINING 1.5 PER CENT Mg₂Si AFTER HEATING THREE DAYS AT 590° C. AND QUENCHING IN WATER.

and at 170° C. Age-hardening curves for the various temperatures are shown together in Fig. 12 for convenience of comparison. Widely different time scales are used necessarily.

During the first 168 hr. of room-temperature aging, the specimens were kept at a constant temperature of 32° C.—slightly above room temperature, for convenience. After this time the temperature followed the normal fluctuations in the laboratory. The lower curve shows on an expanded time scale the first stages of aging at room temperature, while the curve immediately above shows the entire course of room-temperature aging up to three years. In three years the hardness increased from 41 to 82, an increase of exactly 100 per cent.; 62 per cent. of this increase occurred during the first 10 hr. at 32° C. There was a distinct increase in hardness from six months to three years.

The upper curves show the much more rapid increase in hardness at 150° C. and 170° C. The hardness attained at 150° C. appears to be slightly higher than that attained at 170° C. It is also of interest that the hardness did not appreciably decrease after 300 hr. at 150° C. or 65 hr. at 170° C.

The chief commercial alloy[6] of the aluminum-magnesium silicide type made in this country contains 0.6 per cent. magnesium and 1 per cent. silicon, which is sub-

[6] Designated 51S by Aluminum Co. of America.

stantially in excess of that required to combine with all of the magnesium present to form Mg_2Si. The commercial alloy also naturally contains more iron than the high-purity alloys discussed in this paper, and may contain small amounts of other elements, such as copper. One or more of the complex aluminum-iron-silicon constituents is observed in the microstructure but free silicon is seldom seen. It is possible, however, that the solid solution formed during the high-temperature or solution heat treatment contains silicon somewhat in excess of the ratio found in Mg_2Si. If so, such silicon would contribute to the solution hardening effect but precipitation of silicon would not be expected to add greatly to the precipitation hardening effect.[7]

The effect of quenching temperature on the properties of 51S sheet is shown in Table 7. This lot of material contained 1.04 per cent. silicon, 0.65 per cent. magnesium and 0.30 per cent. iron. This represents a magnesium silicide content of 1.03 per cent. with an excess of 0.66 per cent. silicon over that required to combine with the magnesium. Tensile test specimens cut across the grain were heated for periods of $\frac{1}{2}$ hr. in an electric furnace at the various temperatures, and quenched in water. Tests were made within 20 min. after quenching, after aging six days at room temperature, and after a precipitation heat treatment of 18 hr. at 150° C.

The increases in strength on aging shown in Table 7 have been calculated as percentages of the strength immediately after quenching, with the results given in Table 8. Table 8 also shows the solubility of Mg_2Si in the pure binary alloys as estimated from the curve of Dix, Keller and Graham, and the amount of Mg_2Si dissolved at the various temperatures in the particular lot of 51S under consideration, assuming equilibrium. It is recognized that the excess silicon and the impurities in the commercial alloy may affect the temperature-solubility relations on Mg_2Si although it has been reported that excess silicon has little effect. The maximum percentage increase in strength after 18 hr. at 150° C. over that immediately after quenching was attained with a quenching temperature of 480° C. corresponding to solution of 0.9 per cent. Mg_2Si, while the maximum increase on aging six days at room temperature

TABLE 7.—*Properties of 51S Sheet after Quenching from Various Temperatures and Aging*

Quench Temperature, Deg. C.	No Aging		Aged Six Days at Room Temperature		Aged 18 Hr. at 150° C.	
	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
456	19,320	30.8	23,333	25.3	35,410	14.7
480	21,217	30.5	27,693	26.5	40,067	15.5
505	23,633	28.3	33,170	25.8	43,733	17.0
518	25,160	27.8	36,067	27.0	45,537	15.3
548[a]	28,300	28.2	38,840	26.0	46,900	15.6

[a] Although in this series of tests the properties obtained after quenching at 548° C. were somewhat better than those obtained by quenching at 518° C., it should be pointed out that 548° C. is above the temperature range recommended for the heat treatment of this alloy. A normal temperature of heat treatment is about 520° C.

[7] R. S. Archer, L. W. Kempf. and D. B. Hobbs. Heat Treatment of Aluminum-silicon Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 198.

TABLE 8.—*Percentage Increase in Strength on Aging 51S Sheet Quenched from Various Temperatures*

Quenching Temperature, Deg. C.	Solubility, Per Cent.	Amount Mg₂Si Dissolved, Per Cent.	Increase in Strength, Per Cent.	
			After 6 Days at Room Temperature	After 18 Hr. at 150° C.
456	0.8	0.8	21	83
480	0.9	0.9	30	89
505	1.1	1.03	40	85
518	1.2	1.03	44	81
548	1.4	1.03	37	60

occurred with a quenching temperature of 518° C. corresponding to complete solution of the 1.03 per cent. of Mg_2Si present. Longer aging at room temperature might be expected to result in greater increases of strength for the lower quenching temperatures than for the higher quenching temperatures. This would tend to shift the point of maximum age-hardening at room temperature to a lower quenching temperature and therefore a lower solubility of Mg_2Si.

R. F. MEHL, Washington, D. C.—At the risk of riding my own horse closer to its death, I might point out a few features of Mr. Dix's photomicrographs which illustrate the Widmanstätten mode of crystallization of Mg_2Si from the aluminum-rich solid solution. Possibly at first sight this seems a purely academic problem, but it must be that the mode of crystallization is intimately related to the physical properties produced upon the aging of an age-hardening alloy.

In Fig. 5 Mr. Dix shows the Mg_2Si particles to take the form of approximately equiaxed particles. I take it that the field shown in Fig. 5 is all within a single grain—there is no suggestion of grain boundaries. The photomicrograph shows two crystals of approximately hexagonal outline, one in the lower left corner and one in the upper right corner, with sides very nearly parallel. A structure similar to this has been obtained in my laboratory in a Cu-Zn alloy, pure β as quenched, precipitating the γ phase on long reheating. The small grains in this alloy likewise showed on certain samples, depending upon the angle of cut with respect to the orientation of the original β grain, sides very nearly parallel, throughout the whole β grain. The structure is therefore a Widmanstätten structure, and I should like to ask Mr. Dix if all the Mg_2Si particles within the grain shown in Fig. 5 showed this parallelism. If so, they also must be considered as Widmanstätten figures.

Fig. 6 shows an excellent Widmanstätten figure, a structure quite different from that in Fig. 5, doubtless because of different heat treatment. If the structure shown in Fig. 5 is in fact a Widmanstätten structure it is a puzzle why the structures shown in Figs. 5 and 6 should be so different.

Most of the effort in the study of crystallization from solid solutions is expended upon developing structures sufficiently well defined to permit accurate crystallographic measurements—thus in the study of structures similar to that shown in Fig. 6 it is necessary that the precipitate plates be large enough and sufficiently sharply defined to permit an accurate measurement of the angles between the traces of the plates on the surface of polish. The whole difficulty comes in choosing the most suitable heat treatment—occasionally a slow cooling from the homogeneous solid solution field is best, occasionally a quenching and a reheating. It would be interesting if Mr. Dix can say what conditions he has found most favorable for the development in various aluminum alloys of the type of structure shown in Fig. 6.

H. W. GILLETT, Columbus, Ohio.—In the diagram on the magnesium silicide alloys the solubility curve is a curve pretty well down to very low temperatures, whereas Hanson and Gayler's is a curve first and then becomes almost straight.   That would indicate that with their working conditions, if their results represent real equilibrium, the alloys with small amounts of magnesium silicide would not be responsive to age-hardening, whereas those Mr. Dix worked with are responsive. I wonder if the difference is that they did not get at the whole truth through not having cold-worked their alloys prior to heat treatment, or whether the difference in the shape of the curves is due to the impurities in the aluminum used by Hanson and Gayler.

E. H. DIX, JR.—I am not sure whether I interpreted Mr. Archer's remarks correctly in regard to the first curve, which showed an increase in hardness of 67 per cent. in the first 10 hr. at room temperature.   Is this 67 per cent. an increase from, say, the annealed condition?   Does it include the hardening, by putting the material in solution, or is it age-hardening of 67 per cent. in the first 10 hours?

R. S. ARCHER.—I meant to say 62 per cent.   It is an increase in hardness from the as-quenched condition.   There is a fairly minor point that might be mentioned— that this room temperature was maintained artificially at about 30° C. during the first period of aging, simply because it was easier to maintain a constant temperature a little above room temperature than at room temperature, but the difference is slight; it is no warmer than a hot summer day.

E. H. DIX, JR.—Dr. Mehl's question about the difference in the formation of constituents in Figs. 5 and 6 may be answered, I think, by the way those structures were obtained.   The structure of Fig. 5 was obtained by slowing cooling during the interval that this composition was passing across the solubility curve.   The specimen was annealed 72 hr. at 570° and then slowly cooled to 500°.   The composition was 1.23 per cent. Mg_2Si.   This amount would be put in solution at 570° and then would precipitate at a relatively slow rate because of the slow cooling, from 570° to 500°. Thus relatively large particles of Mg_2Si would be formed.

In the case of the other structure, as shown in Fig. 6, the constituent was all in solution and the specimen quenched, so it was substantially held in solution; the specimen was then reheated to a temperature where precipitation and coalescence could take place, but not at the same rate as the other alloy.   If you are looking for the structure of Fig. 6, the way to get it is to quench from solution at high temperature and then reheat to a relatively low temperature.

With respect to the slope of the curve mentioned by Dr. Gillett, I believe that Hanson and Gayler did not anneal for a sufficiently long time at the low temperature.   I do not think it was the influence of purity as much as the fact that time was not given for the reactions which take place relatively slowly at the low temperatures. Possibly at that time the metallographic technique was not sufficiently perfected to detect small particles which may have occurred, even during the time used.   In the tensile property curve shown at the last of this paper, it is very evident that age-hardening does take place with even the smallest percentages of magnesium silicide shown in the paper.

Constitution of High-purity Aluminum-titanium Alloys

By William L. Fink,* New Kensington, Pa., Kent R. Van Horn,* Cleveland, Ohio, and P. M. Budge,* Fairfield, Conn.

The investigation of the phase relations of high-purity aluminum-base alloys is a part of the fundamental research program of the laboratories of the Aluminum Company of America. The results of a number of binary and ternary systems have previously been published in the Transactions of this society. The aluminum end of the binary aluminum-titanium system has been studied.

This system has received relatively little attention. To the authors' knowledge, there are two previous papers on this subject. E. van Erckelens[1] determined the constitutional diagram reproduced in Fig. 1. According to this diagram, the liquidus represents the separation of TiAl₄ (Ti = 30.7 per cent.). He concluded that this is the composition of the compound, because in his work the eutectic horizontal terminated at 30.7 per cent. titanium and the metallographic examination of a sample of this composition revealed only one phase.

According to the constitutional diagram developed by W. Manchot and A. Leber,[2] reproduced in Fig. 2 from data given in their article, the liquidus represents the separation of the compound TiAl₃ (Ti = 37.2 per cent.). The composition of the compound was derived in a manner similar to that utilized by van Erckelens. Moreover, Manchot and Leber confirmed the composition of the compound by analysis of the constituent left as a residue after dissolving the alloys in weak sodium hydroxide solution.

Although these are the only publications describing the constitution of the system, other investigators have studied the composition of the titanium compound. L. Wöhler[3] says that there is a compound TiAl₃ which was later confirmed by W. Manchot and P. Richter[4] and by

* Metallurgical Division, Aluminum Research Laboratories, Aluminum Company of America.

[1] E. van Erckelens; Aluminum-titanium Alloys and the Influence of Titanium upon Aluminum. *Metall und Erz* (1923) **20**, 206.

[2] W. Manchot and A. Leber: Compounds and Alloys of Titanium with Aluminum. *Ztsch. f. anorg. u. allgem. Chem.* (1925) **150**, 26.

[3] F. Wöhler: Titan-aluminium. *Ann. Chem. u. Pharm.* (1860) **113**, 248.

[4] W. Manchot and P. Richter: Aluminum Titanide. *Leibig's Ann. der Chemie* (1907) **357**, 140.

Manchot and Leber as mentioned above. An early investigation by L. Weiss and H. Kaiser[5] described the compound Ti_2Al_3. The composition, $TiAl_4$, determined by van Erckelens was confirmed by Guillet.

It would seem from these results that the constitution of the aluminum-titanium system was not definitely established and that further work was desirable. In view of possible technical applications, this investigation was confined to the extreme aluminum end of the system.
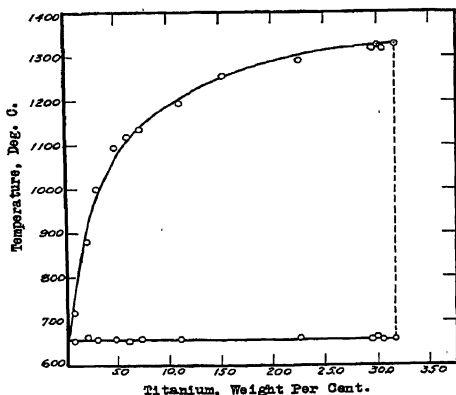
FIG. 1.—ALUMINUM-TITANIUM CONSTITUTIONAL DIAGRAM (VAN ERCKELENS).
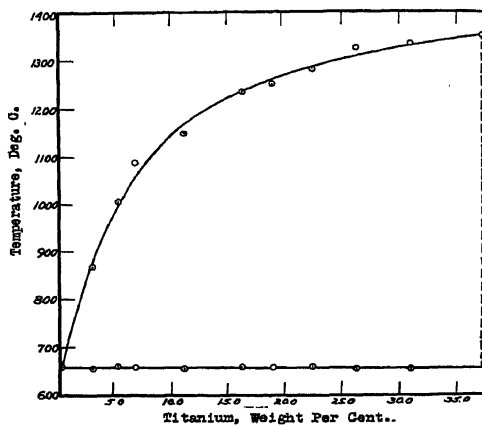
FIG. 2.—ALUMINUM-TITANIUM CONSTITUTIONAL DIAGRAM (MANCHOT AND LEBER).

PREPARATION OF ALLOYS

In general, the alloys used in this work were prepared from electrolytically refined aluminum ingot (99.95 to 99.99 per cent. purity) and titanium-rich alloy. In the preparation of the titanium-rich alloy, the titanium was introduced into high-purity aluminum (99.95 per cent. or better) by means of titanium oxide or potassium titanium fluoride.

In the preparation of the rich alloy by means of the oxide, the aluminum was heated to about 1000° C. or higher in a graphite or plumbago crucible, and a mixture composed of equal parts of cryolite and titanium oxide was introduced. The reaction occurred rapidly and quietly. The metal was removed from the furnace, the freezing of the salt crust accelerated by an air blast, the crust removed and the metal pigged.

The fluoride method was carried out as follows: The salt was mixed with 0.1 per cent. aluminum-bronze powder and pressed into briquettes under a pressure of 80,000 lb. per sq. in. These were introduced into the aluminum heated to 1000° C. or higher. The reaction was quiet and rapid. The salt crust was removed and the metal pigged as in the preceding method.

[5] L. Weiss and H. Kaiser: Metallic Titanium. *Ztsch. f. anorg. Chem.* (1910) **65,** 358.

When a temperature of 1000° C. was used in the preparation of the rich alloy, the maximum amount of titanium introduced was about 2.5 per cent. With higher temperatures, larger amounts of titanium could be introduced. The largest titanium content obtained in this work was 6.3 per cent. However, it is possible to concentrate the titanium by remelting and slowly cooling the alloy. This permits the titanium constituent but not the impurities to settle to the bottom of the melt. Consequently, the amount of impurity per unit of titanium is substantially reduced by using the material from the bottom of such an ingot. The purity of the lower titanium alloys was enhanced by this method of preparation.

An attempt was made to introduce titanium into aluminum by the direct addition of titanium oxide to molten aluminum without the use of cryolite, but this was unsuccessful from a quantitative standpoint. Titanium oxide was added to 99.95 per cent. aluminum at 1000° C. in such an amount that the titanium content of the resulting alloy should have been 0.3 per cent. An analysis of the melt gave a titanium content of 0.03 per cent. Table 1 gives the analyses of the alloys used for thermal curves.

TABLE 1.—*Analyses of Alloys Used for Thermal Curves*

Sample Number	Titanium, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.
4735	1.89	0.14	0.10
4737	1.02		
4778	0.75		
4816	0.64		
4747	0.53		
4776	0.44		
4817	0.41		
4818	0.39		
4748	0.23		
5196	0.15		
4750	0.13		
5197	0.12		
5198	0.06		
5186	0.03		
7714	1.82	0.04	0.08
7715	0.82		
7716	0.37		
7717	0.20		
7718	0.15		
7719	0.12		
7720	0.09		
7810	0.06		
7811	0.03	0.02	0.04

CHEMICAL ANALYSIS OF THE ALLOYS

All the alloys used in this investigation were analyzed for titanium by the usual colorimetric method.[6]   The samples for analysis were milled from ¼ in. thick chill-cast slabs, which were cast at a temperature well above the liquidus.   Each sample of titanium-rich alloy was analyzed for impurities (iron and silicon).

THERMAL ANALYSIS

The investigation of the constitutional diagram of the aluminum-titanium system included thermal analyses of many of the alloys made. In view of results obtained in previous investigations, 600-gram melts
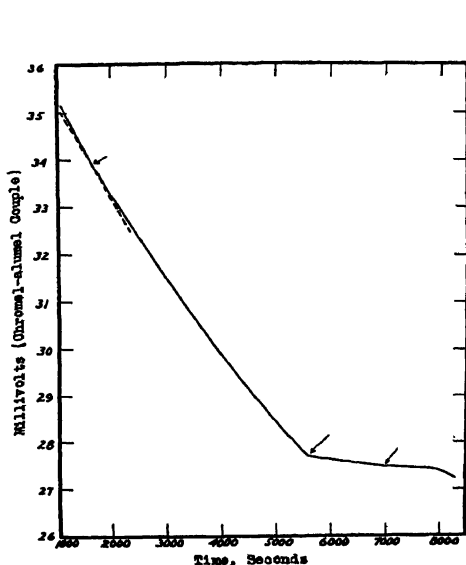
FIG. 3.—TYPICAL TIME-TEMPERATURE CURVE FOR AN ALLOY CONTAINING MORE THAN 0.23 PER CENT. TITANIUM.
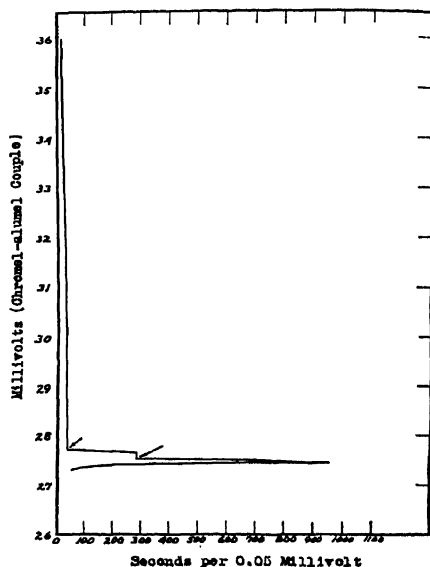
FIG. 4.—TYPICAL INVERSE-RATE CURVE FOR AN ALLOY CONTAINING MORE THAN 0.23 PER CENT. TITANIUM.

were used.   The melt was heated to a temperature well above the liquidus and placed in a small preheated electric furnace.   For the determination of the curve, a Leeds & Northrup precision potentiometer (type K) was used, together with a 22-gage chromel-alumel couple with an iced cold junction, 0° C.   The couple was carefully calibrated against the freezing point of electrolytically refined aluminum (660° C.).   The couple was protected from the melt by a silica tube coated with lamp black.   The furnace was allowed to cool at an average rate of 2° C. per

[6] Standard Methods of Analysis, Alumium Company of America.

minute.   Readings were taken every 0.05 mv. until the more pronounced points were reached, when the readings were taken every 50 seconds.

Cooling curves were taken on 23 different alloys, which were made by diluting titanium-rich samples 4735 and 7714.   It should be noted that alloy 7714 is of higher purity than alloy 4735 (Table 1).   Moreover, sample 7714 was diluted with aluminum of higher purity (99.99 instead of 99.95 per cent.).   Consequently the thermal data obtained from the alloys in series 2 are considered more accurate (Table 2).

With the exception of the curves from samples containing less than 0.23 per cent. titanium, the curves show three points of arrest.   Typical cooling curves are shown in Figs. 3 and 4.   The highest point represents the crystallization of the primary titanium constituent.   The temperature of this point rises rapidly with increasing titanium content.   The other two points are apparently independent of composition in this range, and lie very close together, the one at about 665.1° C. and the other at 659.8° C.

TABLE 2.—*Thermal Points of Aluminum-titanium Alloys*

Sample Number	Primary Point[a] Deg. C.	Second Point Deg. C.	Solidus, Deg. C.
Series 1			
4735	971	664.0	659.5
4737	862	664.5	659.5
4778	817	664.5	659.5
4816	765	664.5	659.5
4747	724	664.5	659.5
4776	733	664.5	659.5
4817	727	665.0	659.5
4818	725	665.0	659.5
4748	696	665.5	659.5
5196		663.5	659.5
4750		662.5	659.5
5197		663.0	659.5
5198		661.5	660.0
5186			659.5
Series 2			
7714		664.7	659.5
7715		665.2	659.7
7716		665.0	659.5
7717		665.4	659.9
7718		664.0	659.9
7719		663.6	660.0
7720		662.9	660.0
7810		660.8	659.8
7811			659.8

[a] As subsequently explained, these temperatures cannot be considered as equilibrium temperatures and were not determined for the alloys of higher purity in series 2.

The cooling curves of the alloys containing less than 0.23 per cent. titanium show two points of arrest. In this range the lower point occurs at 659.8° C., as with samples of higher titanium content. The temperature of the other point gradually decreases from 665.1° C. with diminishing titanium content until at 0.03 per cent. titanium the temperature of the lower point is reached (Figs. 5 and 6).

At first, cooling-curve data were plotted as time-temperature curves and inverse-rate curves. It was apparent that the inverse-rate curve did not show the presence of the primary titanium point. Consequently, subsequent curves were plotted as time-temperature curves. Even on
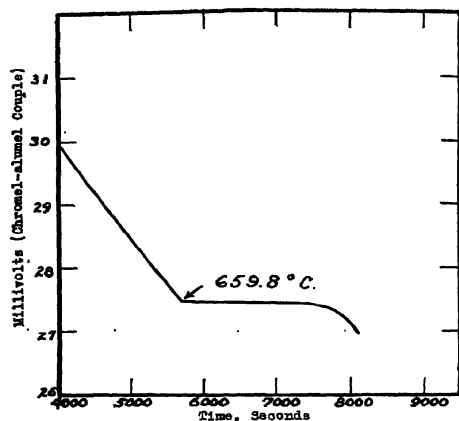
FIG. 5.—TIME-TEMPERATURE CURVE FOR ALLOY CONTAINING 0.03 PER CENT. TITANIUM.
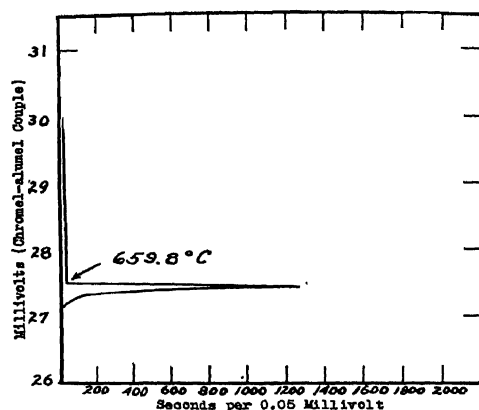
FIG. 6.—INVERSE-RATE CURVE FOR ALLOY CONTAINING 0.03 PER CENT. TITANIUM.

these curves the location of the primary point was sometimes doubtful, particularly for the lower titanium contents. In addition to the difficulties due to the weakness of the point, the alloys undercooled to such an extent that low and erratic results were obtained for the temperature of the primary crystallization.

DETERMINATION OF LIQUIDUS

Because of the fact that the primary point is weak and subject to undercooling in the region investigated, cooling curves were not considered reliable for the determination of the liquidus. Consequently, another method was employed.

Inasmuch as the liquidus is in reality the solubility curve for the titanium constituent in molten aluminum, and the titanium constituent is dense and settles readily, it is possible to use the method that is used

in determining solubility curves for aqueous systems.   This method has previously been applied to the copper-tin system by H. J. Miller.[7]

The procedure was as follows: A charge of 15 lb. of aluminum-titanium alloy, containing approximately 1.5 per cent. titanium, was heated in a Dixon No. 20 plumbago crucible to about 1100° C., thoroughly stirred and placed in a preheated electric furnace at 1100° C., which is above the liquidus of this alloy.   The temperature of the furnace was controlled by a Leeds & Northrup recorder-controller.   The temperature just below the surface of the metal was determined with a calibrated chromel-alumel couple and a portable potentiometer and was found to be constant within ±2° C.

The metal was held at this temperature for 2 hr., after which the dross was removed from the center of the surface and the clean metal allowed to flow into a small ladle preheated to the metal temperature.   Two chilled castings were immediately poured from this sample.   A slab(3 by 1⅞ by ¼ in.) for chemical analysis was cast in an iron mold having a wall thickness of ½ in.   A rod (0.7 in. dia.) for fracture tests and Brinell hardness measurements was cast in a graphite mold.

The temperature was decreased 50° C. and the melt allowed to remain at this temperature, 950° C., for 45 min., to allow the system to reach equilibrium.   The temperature of the metal was determined, a sample was taken and castings were made, as in the previous case.   The temperature was again lowered 50° C. and the procedure repeated.   The time of holding for the lower temperatures was gradually increased to 2 hr. to insure equilibrium.

TABLE 3.—*Composition and Brinell Hardness of Solubility Samples* (*No. 5143*)

Temperature of Equilibrium, Deg. C.	Titanium, Per Cent.	Copper, Per Cent.	Silicon, Per Cent.	Iron, Per Cent.	Brinell Hardness Number, 500-kg. Load, 10-mm. Ball
1011	1.44	0.03	0.11	0.04	
948	1.39				21.8
901	1.06				21.8
846	0.71				21.8
806	0.51				19.7
742	0.32				18.6
700	0.21				17.7
675	0.16				17.5
Surface drillings	0.06				

After the last sample was taken, the melt was allowed to solidify slowly in the furnace.   At the first indication of solidification, the metal

[7] H. J. Miller: The Penetration of Brass by Tin and Solder with a Few Notes on the Copper-tin Equilibrium Diagram. *Jnl.* Inst. Metals (1927) **37**, 188.

was skimmed to remove the dross and any titanium constituent adhering to it.   After complete solidification the top of the ingot was cleaned with a file and drillings were taken for chemical analysis.   The results of the analyses and the Brinell hardness numbers are given in Table 3.

It is evident that the liquidus obtained in this manner lies above that obtained from the cooling-curve data in Table 2.   This is in the direction to be expected in view of the undercooling obtained in thermal analysis. The liquidus curves previously obtained by van Erckelens (Fig. 1) and by Manchot and Leber (Fig. 2) occur at temperatures lower than those of Table 2.   In the range of compositions considered in this report, there

FIG. 7.—STRUCTURE OF AN ALLOY CHILL-CAST FROM LIQUIDUS TEMPERATURE OF 901° C. × 100.

FIG. 8.—STRUCTURE OF AN ALLOY CHILL-CAST FROM LIQUIDUS TEMPERATURE OF 806° C. × 100.

is a disagreement in the liquidus lines determined by Manchot and Leber and by van Erckelens.   It would appear that these differences are due to the undercooling and to the small heat evolution at the primary arrest. At higher titanium contents, where less undercooling would be expected and the heat evolution greater, Manchot and Leber and van Erckelens are in agreement as to liquidus temperatures.

The effect of decreasing amounts of titanium upon the hardness is apparent.   Moreover, the effect of decreasing casting temperature probably tends to counteract to some extent the effect of variation in titanium content.   The hardness of sample 5143, poured at 675° C., approaches that of high-purity aluminum.

METALLOGRAPHIC STRUCTURE

A microscopic examination of the aluminum-titanium alloys revealed the titanium constituent in the form of needles (cross-sections of plates)

distributed through the aluminum matrix. No eutectic structure was observed in any of these alloys. The microstructure of sample 5143 (1.44 per cent. Ti) cast at 901° C. is shown in Fig. 7 and that of the sample cast at 806° C. in Fig. 8. These structures are typical of all the specimens, except that those cast at lower temperatures have fewer and smaller needles.

An interesting metallographic application of the X-ray is given in Fig. 9, which represents a radiograph of a section of a slowly cooled aluminum-titanium ingot. The X-ray reveals TiAl₃ plates (light) extending from the mold walls and dross near the top of the ingot. The dark area near the top of the photograph represents a spongy section formed by shrinkage.

COMPOSITION OF ALUMINUM-TITANIUM CONSTITUENT

A survey of the literature showed that the work of W. Manchot and A. Leber on the composition of the titanium constituent was probably the most reliable and that the formula TiAl₃ represented the composition. However, it seemed desirable to try to confirm their result, because other work had indicated that the composition was either TiAl₄ or Ti₂Al₃.

The method used in this work was substantially the same as that employed by Manchot and Leber. The matrix of a high-purity alloy containing 1 per cent. or more of titanium was dissolved in 5 per cent. sodium hydroxide. The residue was carefully washed, dried and examined under a binocular microscope. Large aluminum-free plates were selected for X-ray and chemical examination.

The average result obtained in eight chemical analyses on the residue of three different samples was 37.3 per cent. Ti. This value checks within the accuracy of the analytical method for TiAl₃ (37.2 per cent. Ti). Since the results are consistent and the residue showed no indication of being attacked by the sodium hydroxide solution, it seems probable that the constituent is the compound TiAl₃. It is of interest to note that the cooling procedure was different for each of the three samples. One sample was a chill-cast rod poured at 901° C., as described under Determination of the Liquidus. Another sample was obtained by slowly cooling an alloy containing about 1 per cent. titanium from above the liquidus to 725° C., holding at this temperature for 5 hr. and pouring the melt into cold water. The third sample was obtained from the bottom of an ingot cooled slowly in the furnace, as described under Determination of the Liquidus.

The residue obtained from the sodium hydroxide treatment was in the form of thin, brittle plates of a silver gray color. When exposed to the air, an iridescent oxide film forms, which protects the plates from further oxidation. As mentioned, the titanium constituent appears as needles on the polished surface. In view of the type of residue obtained, it is

evident that the apparent needles are, in reality, cross-sections of plates. The fact that no plates were found in the polished section is due to the small probability that the polished plane would intersect such a thin plate parallel to its surface.

CRYSTAL STRUCTURE OF TiAl₃

Some of the larger plates of TiAl₃ obtained from a slowly cooled high-purity ingot were selected for the determination of the crystal structure of TiAl₃. All diffraction patterns were made on a General Electric apparatus using a molybdenum target tube operating at 30,000 volts and 20 ma. A Laue pattern was made with the X-ray beam almost normal to one of the plates. The pattern obtained and the gnomonic projection are represented in Fig. 10. The Laue reflections are shown within the large circle at the center, the small full-shaded circles representing reflections of high intensity; half-shaded circles, reflections of medium intensity; and unshaded circles, reflections of low intensity. The projection shows that the crystal is tetragonal with the c axis normal to the plate. An inspection of the pattern showed that the crystal had the symmetry of one of the following classes: $4d$, $4Di$, $4D$, $4e$.

The dimensions of the unit cell were determined by the rotating crystal method, using a cylindrical film. The pattern obtained by rotating the crystal about the c axis gave a value for c_0 of 8.60 Å. The pattern obtained by rotating the crystal about the a axis gave a value of 5.45 Å for a_0. These values of the lattice parameters represent an axial ratio of 1.58, which was used to select the net shown in Fig. 10. The validity of this selection was verified by calculating $n\lambda$ (n = order of reflection, λ =

FIG. 9.—RADIOGRAPH OF SLOWLY COOLED ALUMINUM-TITANIUM INGOT.

wave length) corresponding to each Laue reflection.   No reflections were found that required a wave length less than λ_{min}.

It was thought that a more accurate determination of the lattice parameter could be made by means of the Hull method.   Some of the crystals were reduced to 300-mesh powder and placed in a glass capillary tube with an NaCl standard.   Table 4 gives the values of $\frac{d}{n}$ (interplanar spacing divided by the order of the reflection) greater than 1.30 Å, the
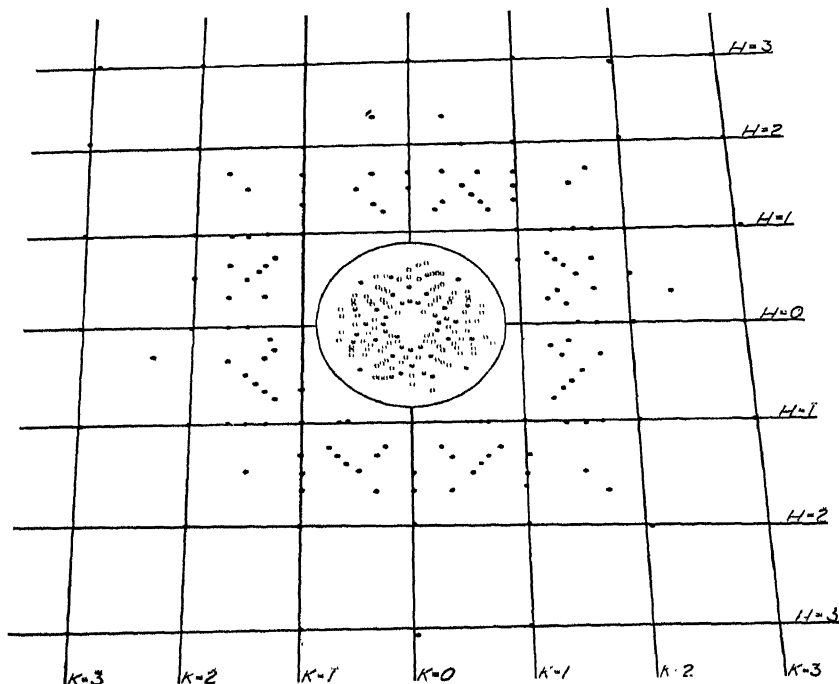
FIG. 10.—DIAGRAMMATIC REPRESENTATION OF LAUE PATTERN AND GNOMONIC PROJECTION.   (X-RAY BEAM ALMOST PARALLEL TO THE FOURFOLD AXIS OF TIAL₃ CRYSTAL.)

estimated and calculated intensities.   The average lattice dimensions obtained from a number of the more intense reflections were $a_0 = 5.424$, $c_0 = 8.574$.   The axial ratio is therefore 1.58.

A density determination of small TiAl₃ plates made by the pycnometer method gave a value of 3.13 grams per cubic centimeter.   Therefore the weight per unit cell is $3.13 \times (5.424)^2 \times 8.574 \times 10^{-24} = 7.90 \times 10^{-22}$.   One TiAl₃ molecule weighs $\frac{129.1}{6.06 \times 10^{23}} = 2.131 \times 10^{-22}$.

Therefore there are 3.71 molecules per unit cell.   Since there must be

an integral number of molecules per unit cell, and since the errors in the density determination would cause low values, the actual number is evidently 4 molecules or 16 atoms.

In order to facilitate the determination of the space group, another Laue pattern was made by inclining the c axis a few degrees to the X-ray beam. The indices of the resulting nonsymmetrical pattern were determined by a gnomonic projection. Table 5 lists the reflections from both Laue patterns having a value of $n \lambda$ between λ_{min}. and $2\lambda_{min}$.; i.e., first order reflections.

TABLE 4.—Powder Reflections for Values of $\frac{d}{n}$ Greater Than 1.30

Miller Indices	Corrected $\frac{d}{n}$	Observed Intensities	Calculated Intensities
002	4.30	0.5	0.4
111	3.50	1.0	1.0
200	2.713+	<0.5	0.28
K_β 113–202	2.58	<0.5	
113–202	2.285	10.0	17.5
004	2.137	3.0	3.6
220	1.91	4.0	5.6
222	1.748	<0.5	0.2
204–131	1.68	0.5	0.54
K_β 224–006	1.60	<0.5	
115	1.566	<0.5	0.15
K_β 400	1.52	<0.5	
133	1.468	<0.5	0.26
224–006	1.429	3.5	5.6
400	1.355	2.5	2.5

TABLE 5.—Indices of Planes Known to Reflect in the First Order
(Laue Patterns)

$\bar{1}95$	$\bar{3}53$	735
$\bar{1}73$	$\bar{1}53$	713
$\bar{1}51$	$\bar{1}75$	533
$\bar{3}73$	$\bar{1}97$	553
$\bar{3}51$	$\bar{9}15$	331
$\bar{5}53$	$\bar{7}13$	
$\bar{3}31$	$\bar{5}11$	
$\bar{7}55$	$\bar{7}\bar{1}3$	
$\bar{7}33$	$\bar{5}33$	

The table shows that only planes having all odd indices reflect in the first order. The absence of all other first order reflections and the

requisite number of equivalent positions would eliminate all space groups except the following:[8]

$$4d - 8 \quad a - d; e, u \neq \tfrac{1}{4}; h, u \neq 0;$$
$$- 9 \quad a - d; e, u \neq \tfrac{1}{4}; f, u \neq 0;$$
$$4Di - 10 \quad i - j, u = \tfrac{1}{4}; o, u = \tfrac{1}{4}, v \neq 0;$$
$$- 14 \quad f - g, u = \tfrac{1}{4}; j, u = \tfrac{1}{4}, v \neq \tfrac{1}{4};$$
$$- 16 \quad c - d; i, u = \tfrac{1}{4}, v \neq 0, \tfrac{1}{2}, \tfrac{1}{4};$$

The space groups $4Di - 10$, $4Di - 14$ and $4Di - 16$ can be eliminated by considering the atomic coordinates and radii. All of these groups require two atomic diameters in $\frac{c_0}{2}$ which would necessitate an improbable compression of the aluminum and titanium atoms.

The remaining special cases of the space groups $4d - 8$ and $4d - 9$ place the atoms in identical positions. In other words, the 16 atoms can be arranged in four groups of four equivalent atoms:

(a) $0, 0, 0; \tfrac{1}{2}, 0, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}, 0; 0, \tfrac{1}{2}, \tfrac{1}{2}.$
(b) $\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, 0; 0, 0, \tfrac{1}{2}; \tfrac{1}{2}, 0, 0.$
(c) $\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}; \tfrac{1}{4}, \tfrac{3}{4}, \tfrac{3}{4}; \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{4}; \tfrac{3}{4}, \tfrac{1}{4}, \tfrac{3}{4}.$
(d) $\tfrac{1}{4}, \tfrac{3}{4}, \tfrac{1}{4}; \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{3}{4}; \tfrac{3}{4}, \tfrac{1}{4}, \tfrac{1}{4}; \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{3}{4}.$

or in two groups of four equivalent atoms and one group of eight equivalent atoms. The eight equivalent positions must be either:

(e) $u \neq \tfrac{1}{4} - 0, 0, u; 0, 0, \bar{u}; \tfrac{1}{2}, 0, \tfrac{1}{2} - u; \tfrac{1}{2}, 0, u + \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}, u;$
$\tfrac{1}{2}, \tfrac{1}{2}, \bar{u}; 0, \tfrac{1}{2}, \tfrac{1}{2} - u; u, \tfrac{1}{2}, u + \tfrac{1}{2};$

or

(h) $u \neq 0 - \tfrac{1}{4}, \tfrac{1}{4}, u; \tfrac{1}{4}, \tfrac{3}{4}, \bar{u}; \tfrac{3}{4}, \tfrac{3}{4}, u; \tfrac{3}{4}, \tfrac{1}{4}, \bar{u}; \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{2} - u;$
$\tfrac{1}{4}, \tfrac{3}{4}, u + \tfrac{1}{2}; \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{2} - u; \tfrac{3}{4}, \tfrac{1}{4}, u + \tfrac{1}{2}.$

Obviously, two groups of eight equivalent atoms are impossible because the titanium and aluminum atoms cannot be considered as equivalent. All the 24 combinations involving (e) or (h) can be eliminated on the basis of insufficient distance between atomic centers.

There now remain four possible arrangements. The titanium atoms at a, b, c or d and the aluminum atoms in the remaining 12 positions. As can be seen by a translation of the origin, all four arrangements are identical. Assuming a slight contraction of the atomic radii, this arrangement has sufficient distance between atomic centers. The increased

[8] R. W. G. Wyckoff and S. B. Hendricks: Die Kristallstruktur von Zirkon und die Kriterien für Spezielle Lagen in Tetragonalen Raumgruppen. *Ztsch. f. Kristallographie* (1927) 66, 73.

R. W. G. Wyckoff: The Analytical Expression of the Results of the Theory of Space Groups. Carnegie Institution of Washington, *Pub.* 318 (1922).

attraction due to compound formation would be expected to slightly
reduce the atomic radii.

In order to confirm this solution, the intensities of the powder reflec-
tions were calculated and compared with the observed intensities.
There was an agreement between the two sets of values as is shown in
Fig. 11.

The application of the theory of space groups to the X-ray data has
resulted in the solution $(4d\ 8 - a,\ b,\ c,\ d)$ of the crystal structure
of TiAl$_3$, which yields X-ray reflections of the observed intensities.
The atomic arrangement is shown by the model represented in Fig. 12.
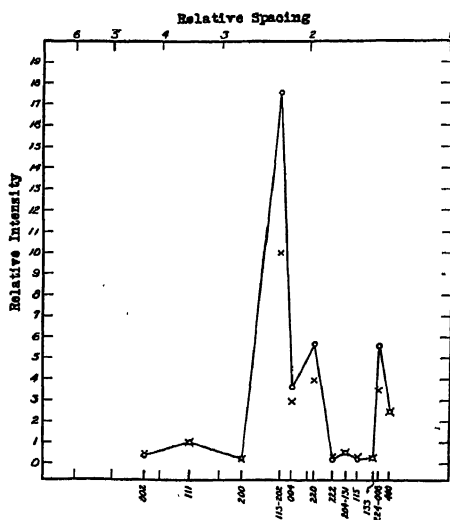
FIG. 11.—RELATIVE INTENSITIES OF
POWDER REFLECTIONS HAVING VALUES OF
d/n GREATER THAN 1.3 Å.
   O = calculated intensities;
   X = observed intensities.
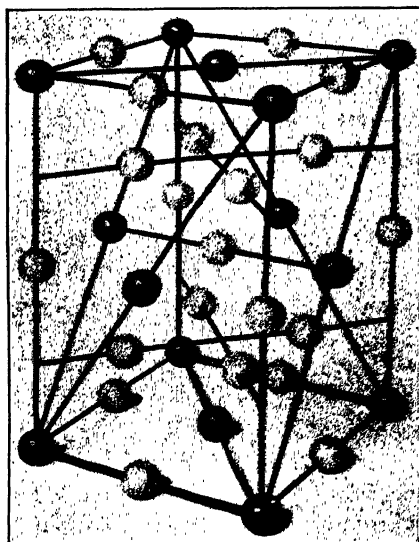
FIG. 12.—MODEL REPRESENTING ELE-
MENTARY CELL OF TiAl$_3$.

ALUMINUM END OF CONSTITUTIONAL DIAGRAM OF
ALUMINUM-TITANIUM SYSTEM

Fig. 13 represents the contitutional diagram from 0 to 1.5 per cent.
titanium as determined in this investigation. The liquidus representing
the primary separation of TiAl$_3$ was determined by solubility measure-
ments and the remainder of the diagram was obtained by thermal
analysis as previously described.

The solidus line occurring at 659.8° C. may represent the solidification
of a eutectic, the composition of which is about 0.03 per cent. titanium,
99.97 per cent. aluminum.

The significance of the line at 665.1° C. has not been determined. It would appear from the diagram that this point might represent a peritectic reaction, the primary TiAl₃ reacting with the aluminum to form another constituent. However, if this were true, one would expect that the composition or crystal structure of the constituent would differ according to the point in the solidification range from which the alloy was quenched. As was mentioned under Composition of Aluminum-titanium Constituent, no change in composition was observed. How-
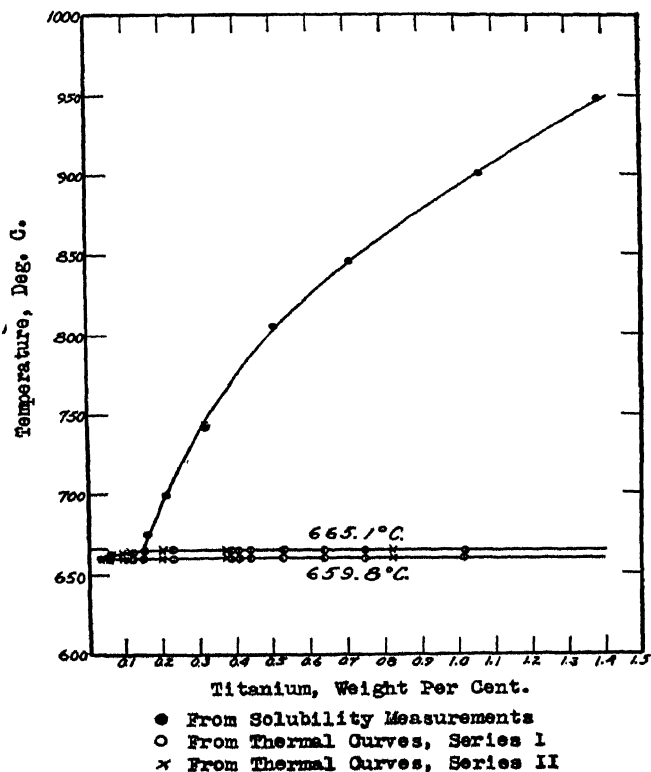
FIG. 13.—ALUMINUM END OF ALUMINUM-TITANIUM CONSTITUTIONAL DIAGRAM.

ever, no sample had been allowed to approach equilibrium at a temperature between the two lower points. Such a sample should contain little or no TiAl₃ if a new compound were formed at the "peritectic" point. Consequently, a small piece from the bottom of the cooling-curve ingot (No. 4778) was heated at 662° C. for 5 hr. This treatment completely spheroidized the titanium constituent. The constituent was separated by solution of the matrix in 5 per cent. sodium hydroxide, as previously described. The impurities could not be separated mechanically because the residue was in the form of a fine

powder.   It was found that the residue contained 35.0 per cent. titanium.   However, deducting from the weight of the sample the weight of impurities found to be present (1.5 mg.), the percentage of titanium in the constituent was found to be 37.0 per cent.   This indicates that the compound is $TiAl_3$.   Diffraction patterns showed that this material had the same crystal structure as the $TiAl_3$ plates.

Another experiment was performed to confirm these conclusions.   A sample was taken from the bottom of an aluminum-titanium ingot (No. 4735) which had been solidified slowly in the furnace.   Six representative samples were analyzed, with the following results: titanium, 2.45 per cent.; copper, 0.03; iron, 0.14; silicon, 0.10.   The sample weighing 3.8619 g. was dissolved in 5 per cent. sodium hydroxide.   The total residue was filtered off, washed, dried and weighed.   The amount of residue to be obtained was calculated, assuming that all of the copper, iron and silicon constituents were decomposed and that only those elements remained in the residue in addition to the titanium constituent. It was further assumed that all the titanium occurred as $TiAl_3$.   With these assumptions, the weight of the residue should be 0.265 g.   The weight of the residue actually obtained was 0.278 g.   This discrepancy probably can be attributed to the fact that the iron and silicon constituents are not completely decomposed by the treatment described, and that consequently some excess aluminum remained in the residue.   If it were assumed that the titanium occurred as $TiAl_4$ or as Ti_2Al_3, the calculated weights of the residues would be 0.318 and 0.185 g. respectively. The indications are that most, if not all, of the titanium is accounted for by the compound $TiAl_3$.

ACKNOWLEDGMENT

The authors express their appreciation to Mr. C. M. Tucker, who made a number of the diffraction patterns and assisted in their interpretation.

DISCUSSION

(C. H. Mathewson presiding)

C. H. MATHEWSON, New Haven, Conn.—Relative to the divided heat effect in the neighborhood of 660° C., it has been suggested that there may be a peritectic transformation at 665° C., but no change in structure could be determined that would correspond to such a change; that is, the titanium-aluminum compound separates along the uppermost curve and has not been observed to change its structure.   However, if we assume that there is some slight solubility of this compound, or of titanium, in aluminum, and that the aluminum-rich solid solution forms peritectically, we might arrive at an explanation of the heat effects observed, which would not necessitate any change in structure as a result of the treatments that have been described.

The occurrence of a divided heat effect as described by the authors would then constitute a departure from true equilibrium conditions.   What I have in mind is

that this compound, having separated out along the upper curve, reacts with the liquid when it reaches 665° C., but that the reaction is incomplete, and there is accordingly envelopment of the titanium compound by the aluminum-rich solid solution.. Thus the process really takes place in two stages; first, there is a peritectic formation of this solid solution which does not take place promptly, we will assume, but owing to insufficient liberation of heat, the temperature falls somewhat while the reaction is going on in this restricted sense, then after the envelopment of the compound by solid solution has become effective, the rest of the liquid solution freezes, virtually at constant temperature, in the form of an aluminum-rich solid solution.   It would seem to be a distinct possibility that cooling curves of the character described would result from a freezing process of this kind.

It might be said relative to this explanation that it would require the melting temperature of aluminum to increase slightly with addition of titanium.   The authors consider that a eutectic is formed at about 0.03 per cent. titanium, but the temperature change involved is something like 0.5°, I believe, and unless very particular attention has been paid to that point, I think it is worth while to consider the above hypothesis a reasonable one.

R. F. MEHL, Washington, D. C.—Professor Mathewson has just said very nearly everything I had in mind to say.   The assumption of a peritectic reaction near the aluminum ordinate would seem to explain all the results, both thermal and crystallographic, which these authors show.   In fact, the thermal analysis results are similar in general form to those on mercury-rich cadmium-mercury alloys upon which Dr. Barrett and I reported several years ago.[9]

There is little doubt that cadmium-mercury alloys rich in mercury undergo a peritectic reaction, and the argument justifying such a reaction in the cadmium-mercury system—upon the basis of lack of equilibrium, as Professor Mathewson suggests—applies also to these new results upon the aluminum-titanium system. A peritectic reaction would require a slight solid solubility of titanium in aluminum, and so far as I know there is no evidence for it.   But the solid solubility curve might well approach the aluminum ordinate rapidly, at temperatures not far below the melting point of aluminum, which would make an experimental demonstration of such a solid solubility very difficult.

YAP, C.-P., New York, N. Y.—Is it not possible to explain the peculiar second thermal arrest by assuming the system to behave as a pseudoternary diagram of Al-TiAl₃-Ti?   From the shape of the solubility line, it seems that the compound is dissociated to an appreciable extent in the melt.   Hence, at any temperature we have Ti in addition to Al and TiAl₃.   If the conditions of the thermal study are such that there was not enough time for the true equilibrium $3Al + Ti = TiAl_3$ to be established, we would then have the equivalent of a ternary system, or a binary system with two kinds of solute.

W. L. FINK.—We thank Professor Mathewson for suggesting a possible explanation for the peritectic arrest.   The lowering of the temperature by addition of titanium is certainly small and might be due to experimental error.   However, through all of the work the thermocouple was constantly checked against the freezing point of high-purity aluminum, so that we are inclined to believe that the observed lowering was real and that there is a eutectic.   We carefully examined the polished sections to see if we could find any indication of eutectic.   We could not find any, but considered it altogether likely that the small quantity of eutectic TiAl₃ might crystallize out on the primary particles.

⁹R. F. Mehl and C. S. Barrett: The System Cadmium-mercury.   *Trans.* A. I. M. E., Inst. Met. Div. (1930) 581, Fig. 2.

W. L. FINK, K. R. VAN HORN AND P. M. BUDGE (written discussion).—Since the presentation of the paper, L. A. Willey has performed some experiments which verify the explanation of the thermal arrest at 659.8° C. which was presented by Professor Mathewson. The diagram is apparently similar to that of the cadmium-mercury system, as Dr. Mehl suggested.

The solid solubility of titanium in aluminum was determined by electrical conductivity measurements and microscopic examination of heat-treated sheet. A series of aluminum-titanium alloys having the compositions listed in Table 6 were chill-cast into 1-lb. ingots and immediately hot-rolled into slabs ¼ in. thick. These slabs were annealed at 575° C. for two days, and cold-rolled to 22-gage sheet (0.025 in.).

O   From Electrical Conductivity Measurements
△   From Microscopic Examination, Solid Solution
✕   From Microscopic Examination, Solid Solution + TiAl₃
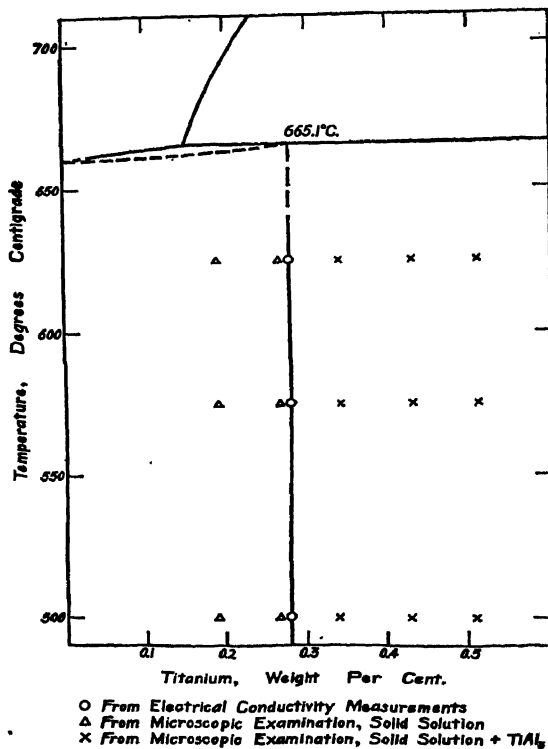
FIG. 14.

The conductivity specimens (0.025 by 0.75 by 20.5 in.) were milled from this sheet. Specimens for microscopic examination were sheared from adjacent sections of the sheet.

Three sets of specimens were suspended within a heavy aluminum block, which was placed in a Leeds & Northrup Homo furnace. The temperature was held at 625° C. for three days and the first series of specimens was removed from the furnace and quenched in water. The temperature was lowered to 575° C. and maintained constant for three days, after which a second set of specimens was quenched. The third group was quenched after holding at 500° C. for four days.

The electrical conductivity was determined at 25° C. by measuring the drop in potential across the specimen and across a standard resistance which was connected

in series. A Leeds & Northrup type K potentiometer was used for these measurements. The conductivity-composition curves exhibited breaks at approximately 0.28 per cent. titanium, regardless of the heat-treating temperature. As the titanium content increased above this percentage the conductivity remained almost constant. This indicates that the solubility of titanium in aluminum is 0.28 per cent. in this temperature range.

Microscopic examination revealed the presence of TiAl₃ in all the specimens containing 0.34 per cent. titanium and above. No constituent could be found in any of the specimens containing 0.26 per cent. titanium or less.

Fig. 14—the extreme aluminum end of the Al-Ti diagram—shows the solubility curve obtained from these conductivity and microscopic results. It is not definitely known whether the solubility is constant over this range or whether the rate of diffusion is so slow that equilibrium was not attained.

Prior to this experiment it had always been thought that the solubility of titanium in aluminum is extremely low, because titanium will settle to the bottom of a melt during slow solidification until the surface layer contains 0.06 per cent. or less of titanium. In order to ascertain whether or not settling can take place without the formation of TiAl₃, a slowly-solidified ingot (1½ in. dia. and 3¼ in. long) containing 0.14 per cent titanium was sectioned for chemical analysis and microscopic observation. The sample from the top of the ingot analyzed 0.05 per cent. titanium, that from the middle 0.14 per cent. titanium, and the one from the bottom 0.23 per cent. titanium. No TiAl₃ particles could be observed even in the sample from the bottom of the ingot. It would seem that the first dendrites to form settle to the bottom and that they contain more titanium in solid solution than is soluble in the melt at that temperature. In this way the supernatant melt is progressively impoverished. No etch has yet been found that will differentiate the dendrites with various titanium contents.

In view of the results just described, it would seem that the diagram represented in Fig. 14 will explain all existing data, and that the pseudoternary hypothesis suggested by Mr. Yap is unnecessary.

TABLE 6.—*Composition of Alloys Used for Solid-solubility Measurements*

Sample No.	Composition, Per Cent.			
	Titanium	Iron	Copper	Silicon
Y4618	0.000	0.005	0.004	0.004
Y4619	0.012	0.005	0.006	0.005
Y4620	0.015			
Y4621	0.036			
Y4622	0.041			
Y4623	0.047			
Y4624	0.069			
Y4625	0.083			
Y4626	0.125			
Y4627	0.167			
Y4628	0.191			
Y4629	0.267	0.006	0.007	0.010
Y4763	0.34			
Y4764	0.43			
Y4765	0.51			
Y4766	0.57			

Experiments on Retarding the Age-hardening of Duralumin

By E. H. Dix, Jr.,* and F. Keller,† New Kensington, Pa.

The desirable high strength and hardness of the heat-treated strong aluminum alloys result from two distinct structural changes: (1) the formation of a solid solution by heating at the required temperature for a sufficient period, and the substantial retention of this solid solution by rapidly quenching; (2) precipitation of particles of constituent and coalescence to a critical size to produce maximum strength and hardness. In alloys of the duralumin type, that is, alloys containing both copper and magnesium silicide precipitation takes place at normal atmospheric temperature, whereas in alloys containing copper without magnesium silicide or magnesium silicide without copper, maximum properties are obtained only after an accelerated aging treatment consisting of heating for 15 to 20 hr. at temperatures of about 150° C.

The mechanical properties of these alloys subsequent to quenching but prior to aging are ideal for forming operations. Unfortunately, however, the alloys of the duralumin type age very rapidly during the first 24 hr. and aging is substantially complete after four days. For severe forming, such as the heading of rivets, it is desirable that this be accomplished within ½ hr. or at the most 2 hr. after quenching.

Alloys containing magnesium silicide without copper also age at normal temperatures but the aging is less rapid and the material can be satisfactorily worked within several weeks after quenching. Some slight aging of alloys containing copper alone also takes place at room temperature but it is unimportant from the standpoint of workability. Any method of retarding the aging at room temperature of the duralumin type of alloys would be of considerable advantage in that the period during which the material could be worked successfully would be lengthened. For instance, in aircraft plants it is customary to supply the workmen with small lots of rivets that should be used within ½ hr. after heat treatment. Such procedure has the obvious disadvantage of being uneconomical, and furthermore there is always the possibility that the workmen would use the rivets after the time limit had expired, or the supply being depleted might use some that had not been heat-

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* Metallurgist, Aluminum Research Laboratories.
† Assistant Metallurgist, Aluminum Research Laboratories.

treated. In the first instance incipient cracks would develop and later open up and cause failure and in the second instance difficulty from corrosion might be experienced.

It has been generally understood for some time that the age-hardening of duralumin could be retarded by storing at low temperatures. It has been the purpose of the present investigation to obtain specific data which could be applied to fabrication methods.

The results show that the age-hardening of duralumin can be satisfactorily retarded for a period of at least 24 hr. by storing the material at a temperature of 0° C. immediately after quenching. The age-hardening of such material proceeds at the normal rate when it is allowed again to reach room temperature, hence all forming operations should be carried out within the usual period after removal from the low-temperature storage. This information makes it possible for an aircraft manufacturer to heat-treat a day's supply of rivets at one time and then, by storing the rivets at approximately 0° C. in a convenient ice-water bath or a refrigerator, have available a supply of rivets in the most workable condition at any time during the day.

THE PRESENT INVESTIGATION

In the course of this investigation the following factors were studied with relation to their effects on age-hardening:

1. Quenching from 505° C. into water at room temperature (25° C.) and aging at room temperature (25° C.).

2. Quenching from 505° C. into ice water at 0° C. and aging at room temperature (25° C.).

3. Quenching from 505° C. into ice water at 0° C. and holding at 0° C. for various periods.

4. Quenching from 505° C. into water at room temperature 25° C. and holding at 0° for various periods.

5. Quenching from 505° C. into iced brine at −9° C. and holding at −9° C. for various periods.

6. Quenching from 505° C. into water at room temperature (25° C.) holding for 4, 8, 24 and 48 hr. in ice water or a refrigerator at 0° C. and subsequently aging at room temperature.

The experimental work consisted in carrying out the above treatments on tensile test specimens of commercial 14-gage (0.064 in.) hard-rolled duralumin sheet and then determining the mechanical properties. The chemical composition of the material was as follows: Cu, 3.92 per cent.; Mg., 0.58 per cent.; Mn, 0.57 per cent.; Si, 0.42 per cent.; Fe, 0.51 per cent.; Al (by diff.), 94.00 per cent. The heat treatment was carried out in a fused nitrate bath operated at a temperature of 505° C. The temperature was kept constant within close limits by means of a potentiometer controller in connection with the crucible furnace used for heating

the nitrate bath. All of the tensile specimens were machined to size and measured prior to heat treatment, in order that the testing might be carried out with as little delay as possible following quenching or removal from storage at low temperatures. The quenching was done

Fig. 1.

as quickly as possible so as to eliminate variations resulting from differences in the rate of quenching.

A mixture of finely cracked ice and water was employed for maintaining the specimens at 0° C. for the shorter intervals, that is, up to 4 hr., while for the longer periods an electric refrigerator was used. In the instance where a quenching and holding temperature of −9° C. was used a mixture of finely cracked ice and brine was employed.

The specimens were tested on an Amsler 20,000-lb. capacity testing machine using Templin's self-aligning grips. The tests were made as rapidly as possible after the specimens were removed from the low-temperature storage. The yield points given in the results were obtained from the Amsler diagrams.

RESULTS OF THE INVESTIGATION

The results of the present investigation indicate that age-hardening can be substantially retarded for at least 24 hr. by maintaining the

QUENCHED IN WATER AT ROOM TEMPERATURE AND AGED AT ROOM TEMPERATURE.

QUENCHED IN ICE WATER AT 0°C AND HELD AT 0°C UNTIL TESTED.

HARDNESS ROCKWELL (E SCALE)

TIME INTERVAL BETWEEN QUENCHING AND TESTING
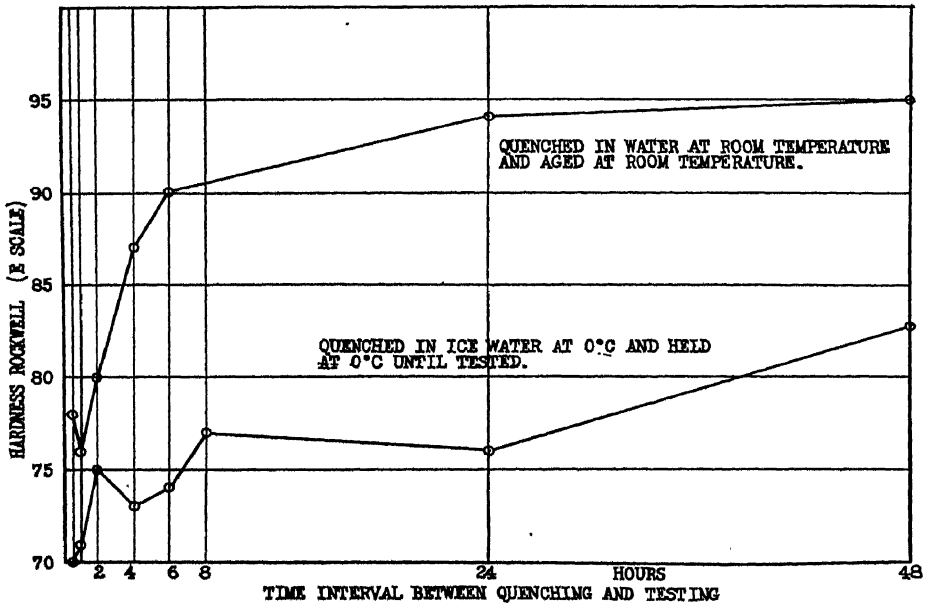
FIG. 2.

material at about 0° C. after quenching. The results obtained by quenching and holding the material in ice water at 0° C. are shown graphically in Fig. 1. In this diagram curves are shown for the same material quenched in water at room temperature and held at room temperature, also for that quenched in ice water at 0° C. and aged at room temperature. Apparently there is very little difference in the values for tensile strength up to 2 hr. after quenching; however, after this interval the values for material held at 0° C. remain constant for 24 hr. while the values for the other two conditions increase fairly rapidly for about 8 hr. and the material after this period possessed about 95 per cent. of the maximum properties obtained when the aging was continued for 96 hr. The yield point values remained practically constant for 24 hr. when the material was quenched in ice water at 0° C. and maintained

at 0° C.   After this interval a slight amount of age-hardening occurred, as tensile strength, yield point and hardness increased uniformly. In the other two conditions the yield point increased at the same rate as the tensile strength.

·The effect of aging on hardness is shown in Fig. 2.   The hardness value (Rockwell E scale) of the material quenched in ice water at 0° C. and held 24 hr. at 0° C. is comparable with the values obtained 1 hr. subsequent to quenching in water at room temperature and aging at
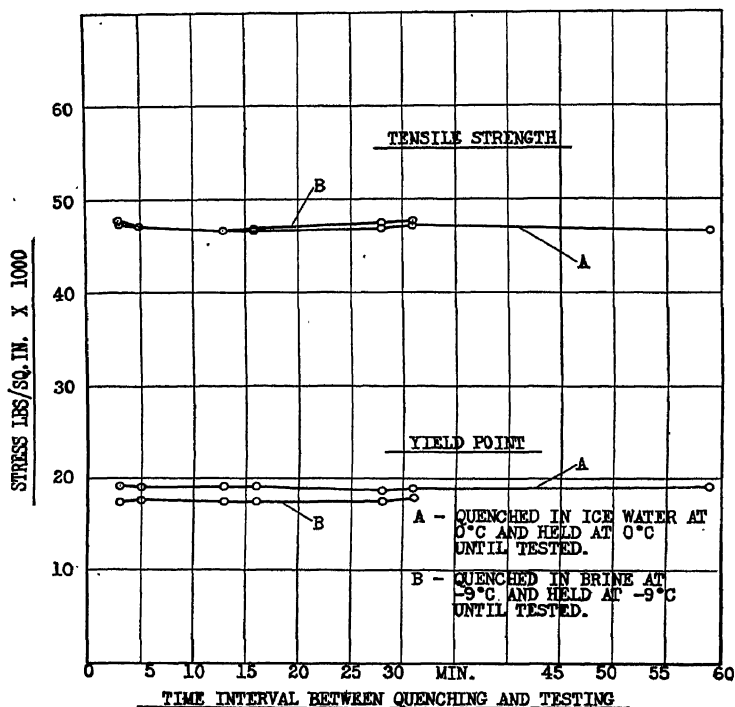
FIG. 3.

room temperature.   It is also interesting to note that immediately after quenching the hardness values of the material quenched in ice water are considerably lower than for the same material quenched in water at room temperature, although the tensile strength and yield point of these two lots are identical.

The results obtained when employing a lower quenching and holding temperature are shown in Fig. 3.   In this instance an ice-brine mixture was used to maintain the desired temperature.   The specimens were quenched in the ice-brine mixture, immediately washed free from salt, and then placed in a container holding kerosene.   The whole container was immersed in the ice-brine mixture.   The temperature of the kerosene

was taken at 5-minute intervals and varied between −8° and −10° C. The two sets of curves in Fig. 3 show that there was practically no change in the rate of aging produced by employing the lower temperature. There was, however, a marked difference in the yield point values, and as the tensile strengths were practically identical the material with
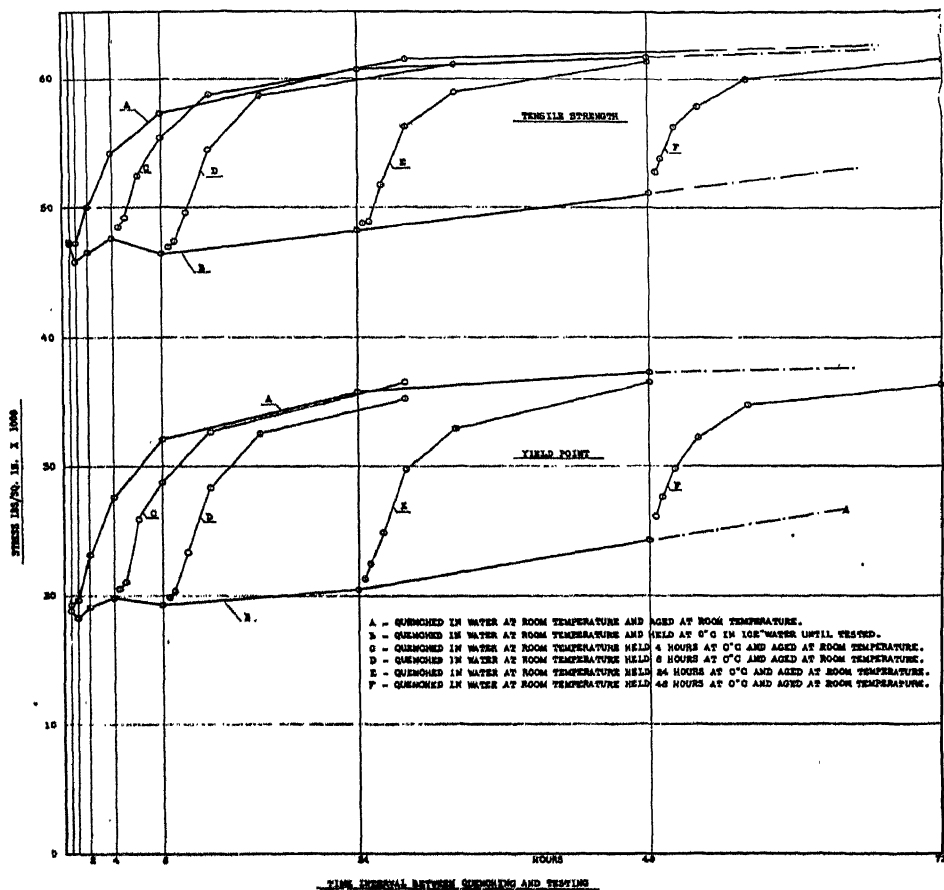
FIG. 4.

the lower yield point should possess the most workability. It is felt that some very important results could be obtained if still lower temperatures were used, and it is our intention to continue the investigation along these lines.

The results shown in Fig. 4 are of the most interest from a commercial viewpoint. In this graph the mechanical property values are compared for material quenched in water at room temperature and aged at room

temperature, and material quenched in water at room temperature and maintained at 0° C. until tested.   In the latter instance it should be noted that, even though the material was quenched in water at room temperature, the storage at the low temperature had substantially retarded age-hardening for at least 24 hr.   These two sets of curves are marked *A* and *B* respectively on the graph.   Curves *C*, *D*, *E* and *F* represent material quenched in water at room temperature and maintained at 0° C. for 4, 8, 24 and 48 hr. respectively and then allowed to age for various periods at room temperature.   Thus, for instance, the first point on curve *C* indicates that the material was tested $4\frac{1}{2}$ hr. after quenching but the material was held at 0° C. for 4 hr. of this period and then aged $\frac{1}{2}$ hr. at room temperature.   These same data apply to the first points on curves *D*, *E*, *F* except that in these instances the holding time was 8, 24 and 48 hr. respectively.

The rate of age-hardening, as shown by the slope of the tensile strength and yield point curves *C*, *D*, *E* and *F*, is apparently the same whether the material has been held at 0° C. for 4, 8, 24 or 48 hr. subsequent to aging at room temperature.

Inasmuch as age-hardening proceeds at the normal rate when the material again attains room temperature, it is imperative that severe forming operations be carried out within the usual periods of $\frac{1}{2}$ to 2 hr. subsequent to removal from the low-temperature storage.

ACKNOWLEDGMENT

DISCUSSION

(H. W. Gillett presiding)

F. KELLER.—The experiments described in this paper were started as a result of a rather interesting incident.   Several years ago, I believe, the heat treatment of duralumin rivets was being carried out at one of the aircraft plants in Buffalo, and somehow the basket or container of rivets was placed outdoors on a window sill after quenching.   The temperature was low, 20° F.   I assume that the rivets were forgotten the day they were quenched.   When the men used the rivets the next day they were able to head them up with as much ease as if they had done it immediately after quenching.   Mr. Clements, of the Curtiss Airplane and Motor Corpn., reported this observation to Mr. Archer, who in turn called our attention to the fact.   However, at that time we did not do any work on this problem.

Recently several other aircraft manufacturers heard that it was possible to retard the age-hardening of duralumin by keeping the duralumin at a low temperature after quenching, and they took this up with one of our sales representatives, who referred the question to the Aluminum Research Laboratories.   Having no definite infor-

mation on this subject, we decided to carry out a few simple experiments to determine whether the age-hardening of duralumin could be retarded, and if such a method to retard the age-hardening would be suitable for use in commercial practice.

H. W. GILLETT, Columbus, Ohio.—It is interesting to note that this was an outcome of shop observation. It points the moral that no matter how extensive our research may be, we cannot afford to neglect the sensible observations of the men in the shop.

Aluminum-silicon-magnesium Casting Alloys

By R. S. Archer* and L. W. Kempf,* Cleveland, Ohio

The binary aluminum-silicon alloys have certain characteristic advantages which are now well known, and these alloys have come into considerable use during the past several years.[1] Their field of application has been limited to a certain extent, however, by their low yield point and hardness, low endurance limit, and relatively poor machining characteristics. These properties are improved by the addition of copper, and the ternary aluminum-silicon-copper alloys constitute an important class. The addition of copper decreases the corrosion resistance of the aluminum-silicon alloys and increases specific gravity. Magnesium is a hardening addition which seems to have relatively little effect on corrosion resistance, and which, of course, reduces specific gravity.

The object of the work described in this paper was the development of alloys and heat treatments for the production of sand castings and permanent-mold castings having substantially all the advantages of the binary aluminum-silicon alloys together with mechanical properties improved to a degree permitting wider application.

Constitution of Alloys

Magnesium and silicon combine in aluminum alloys as the compound Mg_2Si, which forms a binary system with aluminum. In alloys containing an excess of silicon over that required to form the compound, solidification ends with the freezing at 1022° F. (550° C.) of a ternary eutectic of aluminum, Mg_2Si, and silicon. Judging from the horizontal projection of the liquidus surface as given by Hanson and Gayler,[2] this ternary eutectic contains about 13 per cent. silicon and 6 per cent. magnesium. All of the alloys discussed here contain excess silicon, so it

* Aluminum Research Laboratories, Aluminum Co. of America.

[1] The Aluminum Industry, 2, 154–166, 202–215. McGraw-Hill Book Co. New York, 1930. Also R. S. Archer and L. W. Kempf: Modification and Properties of Sand-cast Aluminum-silicon Alloys. *Trans.* A. I M. E. (1926) **73**, 581; *Jnl.* Inst. Metals (1926) **35**, 539.

[2] D. Hanson and M. L. V. Gayler: The Constitution and Age Hardening of the Alloys of Aluminum with Magnesium and Silicon. *Jnl.* Inst. Metals (1921) **26**, 321.

will be unnecessary to consider the constitution of the alloys containing an excess of magnesium over that required to form Mg_2Si.

In the binary aluminum-silicon alloys the solid solubility of silicon decreases from 1.6 per cent. at the eutectic temperature, 1071° F. (577° C.), to 0.05 per cent. at room temperature. In the binary aluminum-Mg_2Si system, the solubility of the compound decreases from 1.8 per cent. at the eutectic temperature, 1103° F. (595° C.), to 0.1 per cent. at room temperature. According to Hanson and Gayler, an excess of silicon has little effect on the solubility of Mg_2Si.

THEORY OF HEAT TREATMENT

The binary aluminum-silicon alloys can be materially hardened by solution heat treatment.[3] (Table 1.) Strength and hardness can sometimes be increased by well over 50 per cent. by quenching from near the eutectic temperature as compared with cooling slowly. This hardening is accompanied by decreased plasticity and usually by decreased elongation. In alloys containing more than 1.6 per cent. silicon, a spheroidizing effect accompanies the solution effect.[4] In wrought alloys and modified cast alloys, the solution effect apparently reaches a maximum in relatively short times of heat treatment. Treatment for a short time near the eutectic temperature therefore favors hardening while treatment for a long

TABLE 1.—*Effect of Heat Treatment on the Physical Properties of a Normal Sand-cast Aluminum-silicon Alloy*

(Archer, Kempf and Hobbs)

Sample 4911; Copper, 0.07 Per Cent.; Iron, 0.24 Per Cent.; Manganese, Nil; Silicon, 4.99 Per Cent.

Condition	Yield Point Lb. per Sq. In	Tensile Strength Lb. per Sq. In	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg., 10 Mm.
As cast................................	.	19,730	9.5	
As cast, 30 days at room temperature..	7,850	19,430	9.5	37.1
Heated 30 min. at 565° C., quenched..		23,190	16.3	42.4
Heated 20 hr. at 565° C., quenched....		22,020	22.5	40.2
Heated 75 hr. at 565° C., quenched....	7,870	21,560	25.2	37.9
Heated 75 hr. at 565° C., slowly cooled	4,310	13,780	32.5	24.8
Heated 75 hr. at 565° C., quenched, aged 28 days at room temperature..	8,040	21,630	25.3	38.1
Aged 75 hr. at 565° C., quenched, aged 100 hr. at 150° C.................	9,700	21,550	20.2	40.4

[3] R. S. Archer, L. W. Kempf and D. B. Hobbs; Heat Treatment of Aluminum-Silicon Alloys. *Proc.* Inst. Met. Div. A. I. M. E. (1928) 198; *Jnl.* Inst. Metals (1927) **38**, 411.

[4] Z. Jeffries and R. S. Archer: U. S. Patent 1508556. Applied for Jan. 4, 1921; issued Sept. 16, 1924.

time causes some loss of hardness resulting from spheroidizing of silicon, but increases plasticity.

There is no appreciable age-hardening effect at room temperature in aluminum-silicon alloy castings either as cast or after solution heat treatment. A study of age-hardening in a wrought alloy containing 2.8 per cent. silicon showed increases up to 15 or 20 per cent. after various precipitation treatments. In general the binary aluminum-silicon alloys have not been considered capable of useful age-hardening. Their stability is an advantage when it is desired to retain the original plasticity and ductility.

The properties of the binary aluminum-Mg₂Si alloys are affected to a remarkable degree by heat treatment. A commercial alloy of this type containing 1.0 per cent. silicon and 0.6 per cent. magnesium is in wide use in this country for wrought products. Strictly speaking, there is in this alloy an excess of 0.65 per cent. silicon over the amount required to form Mg₂Si. Some of this excess may be combined with iron to form one or more ternary constituents of low solubility. It seems, however, that enough silicon goes into solid solution during the high-temperature treatment to contribute materially to the solution hardening effect although it probably contributes but little to the precipitation hardening. The properties of this material in various conditions will illustrate the effect of heat treatment of the aluminum-Mg₂Si alloys (Table 2).

TABLE 2.—*Properties of Wrought Alloy Containing* 1.0 *Per Cent. Silicon and* 0.6 *Per Cent. Magnesium*

Heat Treatment	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Hardness, Brinell 500 Kg., 10 Mm.
	Lb. per Sq. In.			
Annealed at 650° F.	5,500	16,000	30	28
Quenched from 970° F.[a]	20,000	35,000	24	64
Quenched from 970° F., aged at 300° F.	35,000	48,000	14	95

[a] Followed by aging several days at room temperature.

PREVIOUS WORK ON CASTINGS

In the course of the work leading to the development of the commercial wrought alloy containing 1.0 per cent. silicon and 0.6 per cent. magnesium, some tests were made on castings. One case which has been previously described[5] was that of an alloy containing 1.75 per cent. silicon and 1.0 per cent. magnesium. When cast in the form of a permanent-mold test bar of ½ in. dia., this alloy had a tensile strength of 20,000 lb. per sq. in., an elongation of 5 per cent. in 2 in. and a Brinell

[5] R. S. Archer and Z. Jeffries: U. S. Patent 1472739. Application filed Dec. 20, 1921; patent issued Oct. 30, 1923.

hardness of 60. After heating about 15 hr. at 550° C. and quenching, the strength was increased to 36,000 lb. per sq. in., the elongation to 16 per cent. and the Brinell hardness to 67. Precipitation heat treatment ("artificial aging") for 15 hr. at 150° C. raised the strength to 50,000 lb. per sq. in. and the Brinell hardness to 123, while the elongation was decreased to 5.5 per cent.

Among tests which were made subsequently, of which the results have not been published, those on two alloys of high purity, cast in sand and heat-treated, may be mentioned. Electrolytically refined aluminum ingot of 99.95 per cent. purity was used in making these alloys. Bars ½ in. dia. were poured in green-sand molds of the usual form at 1250° F. (675° C.), heated 40 hr. at 1022° F. (550° C.), quenched and tested after aging five days at room temperature. The average results were as shown in Table 3.

TABLE 3.—*Properties of Alloys of High Purity*

Alloy	Si	Mg	Yield Strength	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness
			Lb. per Sq. In.			
A	0.87	0.62	15,970	32,460	18.3	62.4
B	3.0ᵃ	0.6ᵃ	16,550	31,975	9.7	65.5

ᵃ By mixture.

The high elongation of alloy A in combination with good strength and certain other desirable properties is especially interesting. Unfortunately, it is rather difficult to make commercial castings from an alloy of this composition.

The properties of certain sand-cast alloys of the aluminum-silicon-magnesium system have been investigated by the Materials Section, Engineering Division, Air Service, U. S. A.[6] The results obtained are illustrated by the values in Tables 4 and 5, taken from the last two of the papers by Daniels. It is of interest to note especially the properties of melts 2824 and 2825 in Table 4, since these are the only ones that ordinarily would be considered as having good casting properties. Both of these compositions in the heat-treated condition gave tensile strengths around 30,000 lb. per sq. in. with elongations around 5 per cent. The iron content of these melts was 0.57 to 0.60 per cent. Table 5 shows that strengths around 30,000 lb. per sq. in., with elongations around 8 per cent., were obtained from melts 2827 and 2832. In Daniels' opinion, "melt 2828, not a magnesium silicide alloy but with about 1

[6] S. Daniels: *Jnl. Ind. & Eng. Chem.* (1924) **16**, 1243; (1925) **17**, 485; (1926) **18**, 393; and (1926) **18**, 1280.

per cent. each of magnesium and silicon, is the most interesting alloy in the series, possessing, after quenching and aging, an ultimate strength of about 34,000 lb. per sq. in. and an elongation of about 6 per cent."

TABLE 4.—*Chemical Analysis and Mechanical Properties of Aluminum-silicon-magnesium Alloys (Daniels[a])*

Melt	Fe, Per Cent.	Si, Per Cent.	Mg, Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Specific Gravity
AS SAND-CAST							
2821	0.44	0.27	0.48	16,450	14.3	30	2.64
2822	0.60	0.49	0.55	17,460	7.3	34	2.64
2823	0.60	0.91	0.54	15,440	3.0	41	2.62
2824		2.90	0.61	20,150	2.8	48	2.62
2825	0.57	4.67	0.56	21,410	3.0	48	2.60
AS QUENCHED AND AGED[b]							
2821				18,900	15.7	34	2.64
2822				27,250	10.7	51	2.64
2823				29,360	5.5	63	2.60
2824				30,550	5.0	65	2.63
2825				30,600	4.8	59	2.60
AS ANNEALED[c]							
2821				11,680	27.5	22	2.64
2822				11,790	20.5	22	2.64
2823				11,050	16.2	21	2.61
2824				5,120	2.0	15	2.38
2825				5,810	2.8	15	2.35

[a] S. Daniels: Properties of Some Sand-cast Alloys of Aluminum Containing Silicon and Magnesium. *Ind. & Eng. Chem.* (1926) **18**, 393–398.

[b] These specimens were heated 96 hr. at 1025° F., quenched in cold water and directly aged for 8 hr. at 300° F.

[c] These specimens were heated 96 hr. at 1025° F. and cooled in the furnace over a period of seven days, down to room temperature.

Daniels also writes, " . . . it will be seen that, for an alloy to be used in the cast state the best combination of strength and ductility attaches to a very low magnesium silicide content, which condition in itself does not make for good casting qualities."

TABLE 5.—*Chemical Analysis and Mechanical Properties of Aluminum-Mg₂Si Alloys (Daniels[a])*

Melt	Mg, Per Cent.	Si, Per Cent.	Fe, Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Specific Gravity
				As Sand-cast			
2826	0.46	0.34	0.58	16,820	15.2	30	2.64
2827	0.90	0.47	0.58	18,160	5.0	40	2.64
2832	0.98	0.66		16,710	5.5	36	2.64
2828	1.16	1.02	0.56	17,870	3.0	48	2.63
2915	1.7[b]	1.00[b]		18,710	2.2	48	2.62
2896	3.85	1.98		19,360	2.0	47	2.58
2830	5.38	2.92		18,690	1.5	50	2.53
2831	8.81	4.95		17,240	1.3	50	2.48
				As Quenched and Aged[c]			
2826				17,890	14.3	31	2.64
2827				29,930	9.2	60	2.64
2832				29,910	8.3	61	2.64
2828				34,110	6.3	65	2.63
2915				24,750	6.5	56	
2896				20,530	2.8	53	
2830				24,700	0.9	66	2.49
2831				14,760	1.0	59	2.37
				As Annealed[d]			
2826				11,860	26.7	20	2.64
2827				11,280	20.2	20	2.64
2832				11,880	17.7	22	2.64
2828				11,570	14.0	22	2.62
2915							
2896							
2830				9,000	5.3	24	2.50
2831				7,070	2.8	22	2.43

[a] S. Daniels: Properties of Some Sand-Cast Aluminum-Magnesium Silicide Alloys. *Ind. & Eng. Chem.* (1926) **18**, 1280–1285.

[b] Calculated.

[c] These specimens were heated 96 hr. at 1025° F., quenched in cold water and directly aged for 8 hr. at 300° F.

[d] These specimens were heated 96 hr. at 1025° F., and cooled in the furnace over a period of seven days, down to room temperature.

EXPERIMENTAL METHODS AND MATERIALS USED IN PRESENT INVESTIGATION

Alloys studied in this investigation were made from three different grades of ingot: (1) commercially pure (99.2 per cent.) aluminum containing about 0.4 per cent. iron, 0.25 per cent. silicon, 0.15 per cent. copper; (2) selected high-purity Hall process ingot, about 99.7 per cent. pure; and (3) electrolytically refined ingot 99.85 per cent. pure. The silicon-rich alloy (15 per cent. silicon) used for test bars was made by dissolving commercially pure (1 per cent. iron) silicon in electrolytically refined aluminum. Copper-rich (33 per cent.) and iron-rich (10 per cent.) alloys used for copper and iron additions were made similarly, using cathode copper and Armco iron. The commercial castings were made

FIG. 1.—METHOD OF MOLDING SAND-CAST TEST BARS.

from Hall process aluminum ingot and commercial silicon-rich alloy (15 per cent. silicon) made by the addition of silicon to the reduction pots.

For the test bars, melting was carried out in plumbago crucibles in a gas-fired crucible furnace. The melts for the commercial castings were made in whitewashed iron pots in tilting gas-fired furnaces. Fig. 1 shows the method of molding the sand-cast bars employed in this work. Both the sand-cast and permanent-mold test bars were cast to size, the test section having a diameter of $\frac{1}{2}$ in. with a length of $2\frac{1}{4}$ in. between fillets. Elongation was measured on a gage length of 2 in. The ends of the test bars were $\frac{3}{4}$ in. dia. All test bars were tested without machining on either a 10,000-lb. Riehle or a 50,000-lb. Olsen testing machine, using self-aligning grips. The Brinell hardness determinations were usually made with a 500-kg. load, although a few determinations were made with a 1000-kg. load. In either case, a 10-mm. ball was used and the load was imposed for 30 sec. The yield strength was taken as the stress required to produce an extension under load of 0.5 per cent. on a 2-in. gage length. A Riehle extensometer reading directly to 0.0002 in. was used in making these determinations.

Heat treatment of the test bars was carried out in an electric furnace with reversed air circulation. Temperature was controlled automatically

and recorded by an instrument of the potentiometer type. The heat-treated bars were aged to constant hardness at room temperature before testing. This aging at room temperature was usually complete within four days. The increase in hardness generally amounted to about 10 points Brinell.
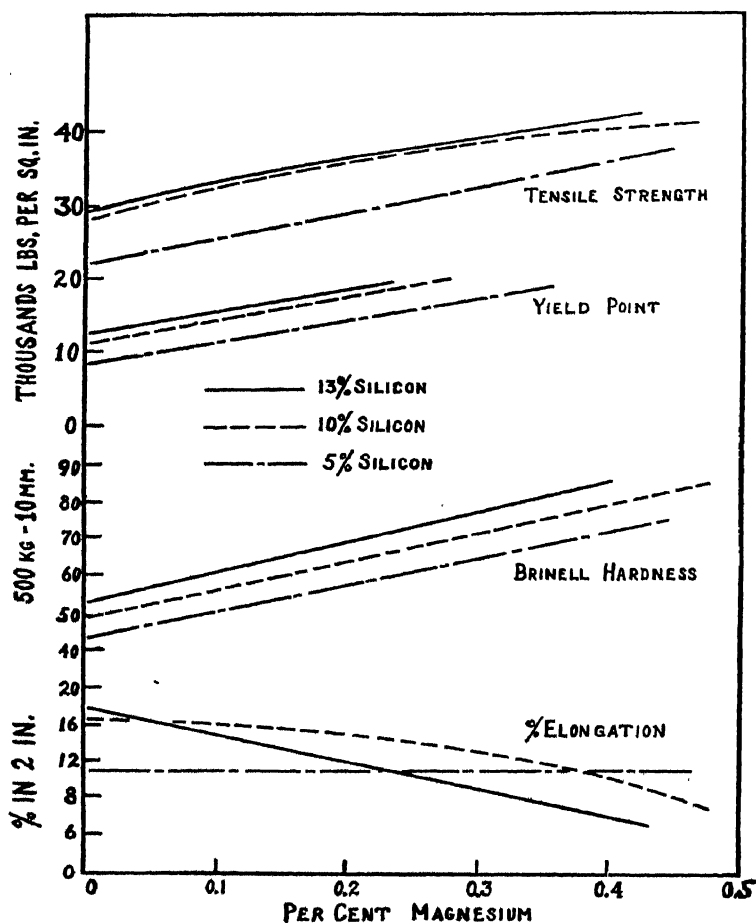
FIG. 2.—EFFECT OF MAGNESIUM ON MECHANICAL PROPERTIES OF SOME CHILL-CAST HEAT-TREATED ALUMINUM-SILICON ALLOYS.

Quenched from 2 hr. at 1025° F., aged four days at room temperature prior to testing. Iron about 0.4 per cent.; copper about 0.15 per cent.

It is to be kept in mind that the results given in this paper were obtained on a laboratory basis and that the physical properties obtainable in regular commercial production may be somewhat lower. Upwards of 90 heats and 1500 individual test specimens were made in this investigation, however, so the values given should be indicative of the results

obtainable with these alloys under good casting conditions.   Averages of most of these tests are included in the tables.   The discussion following is based principally on the accompanying curves, which are graphic representations of typical groups of data.   Not all of the tabulated data are reproduced graphically and the tables should be consulted for details.
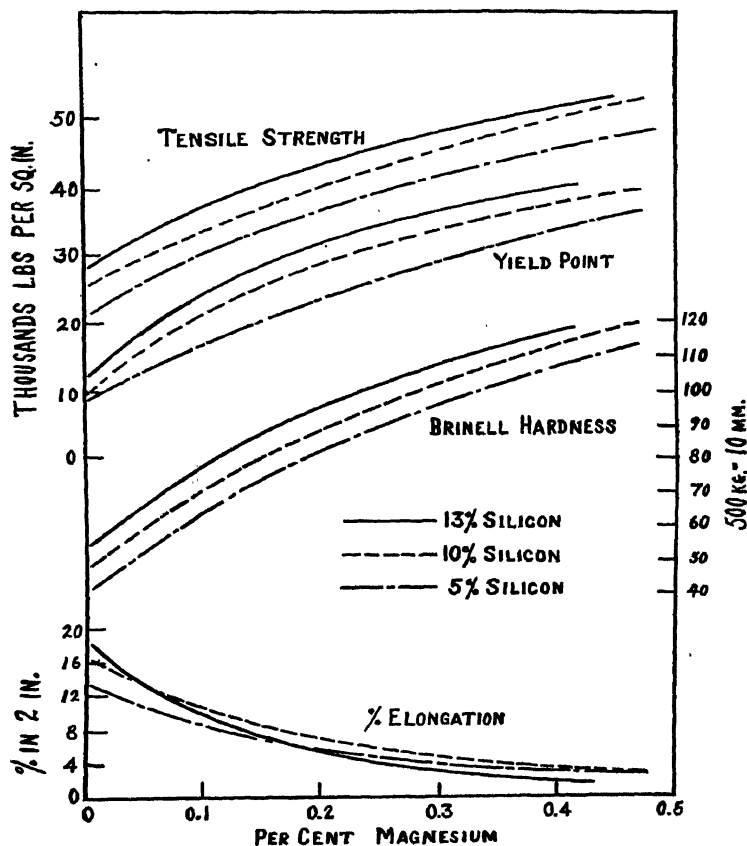
Fig. 3.—Effect of magnesium on mechanical properties of some chill-cast heat-treated aluminum-silicon alloys.
The alloys of Fig. 2 quenched from 2 hr. at 1025° F. and aged 20 hr. at 310° F.

The curves are generally plotted from the composition by mixture, principally because complete analyses were not considered necessary and are thus not available on all alloys.

Effect of Chemical Composition on Mechanical Properties

Magnesium.—The addition of small amounts of magnesium to binary aluminum-silicon alloys results in increasingly harder alloys.   Tensile strength may or may not be increased with initial small additions, depend-

ing on the silicon content and the method of casting. The hardness increases rapidly at first and more slowly with concentrations higher than about 0.50 per cent. magnesium. The elongation decreases continuously. These effects are illustrated in Table 6. In this alloy, the smallest addition of magnesium causes a decrease in tensile strength, probably because
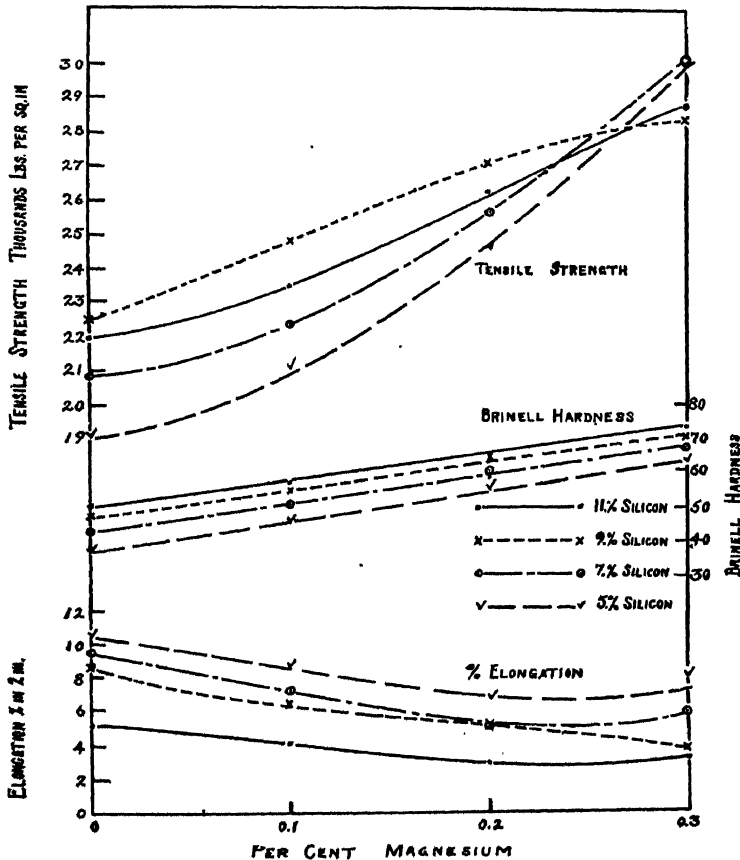
FIG. 4.—EFFECT OF MAGNESIUM ON MECHANICAL PROPERTIES OF SOME SAND-CAST HEAT-TREATED ALUMINUM-SILICON ALLOYS.

Quenched from 20 hr. at 1025° F.; aged three days at room temperature. Data taken from Table 7.

of its coarsening effect on the modified structure produced by chill casting. The hardening effect of the smaller magnesium additions is even more pronounced in sand castings.

As pointed out above, the aluminum-silicon-magnesium alloys are more susceptible to hardening by solution heat treatment than are the binary aluminum-silicon alloys. The curves of Fig. 2 show the effect
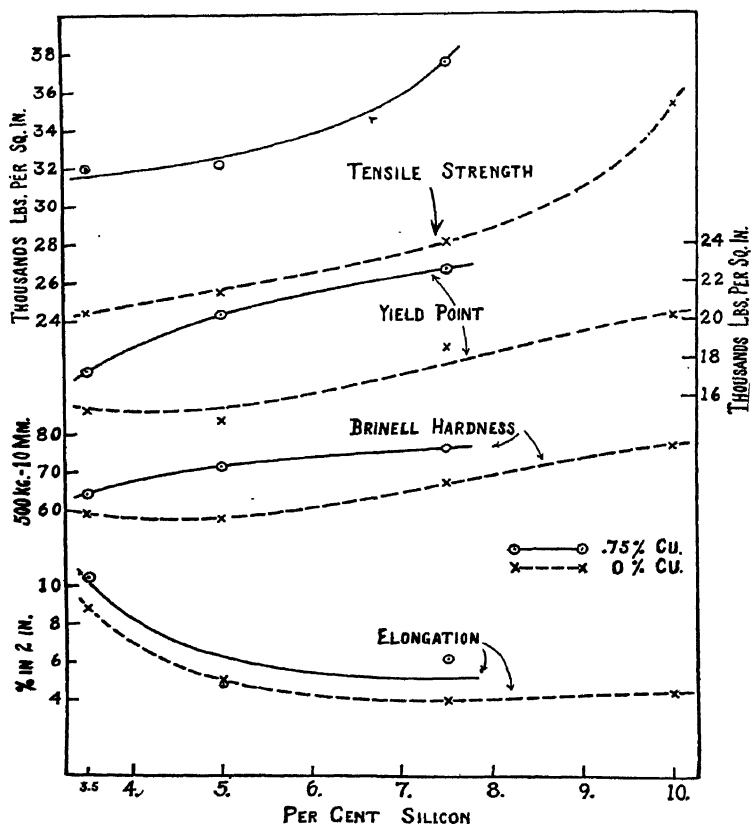
Fig. 5.—Effect of Silicon Content on Mechanical Properties of Some Heat-
Treated Aluminum-Magnesium-Silicon Alloys.

Quenched from 20 hr. at 1000° F.; aged four days at room temperature prior to
testing. Iron about 0.2 per cent.; magnesium about 0.35 per cent.

Table 6.—*Effect of Magnesium on the Mechanical Properties of a Chill-
cast 12 Per Cent. Silicon Alloy*[a]

Cast at About 1350° F. and Tested After Aging Three Days or More at
Room Temperature

Sample	Percentage Composition				Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 1000 Kg., 10 Mm., 30 Sec.
	Cu	Fe	Si	Mg			
4243	0.3[b]	0.5[b]	12.17[b]	0.0	34,550	7.0	67.0
4244	0.3[b]	0.5[b]	11.85	0.08	31,430	6.0	72.0
4245	0.3[b]	0.5[b]	12.04	0.14	31,580	4.0	73.0
4254	0.3[b]	0.5[b]	11.92	0.32	30,680	4.0	77.0
4247	0.3[b]	0.5[b]	12.08	0.47	31,550	1.5	83.0
4248	0.3[b]	0.5[b]	12.17[b]	1.08	29,500	1.5	87.0

[a] Values given are averages of five or more tests.

of increasing magnesium concentrations on the tensile properties of some heat-treated chill-cast alloys, containing 5, 10 and 13 per cent. silicon. These curves are based on the results of scattered tests made over a considerable period of time.   Points representing specific tests on definite compositions are not indicated.   The curves represent what are con-
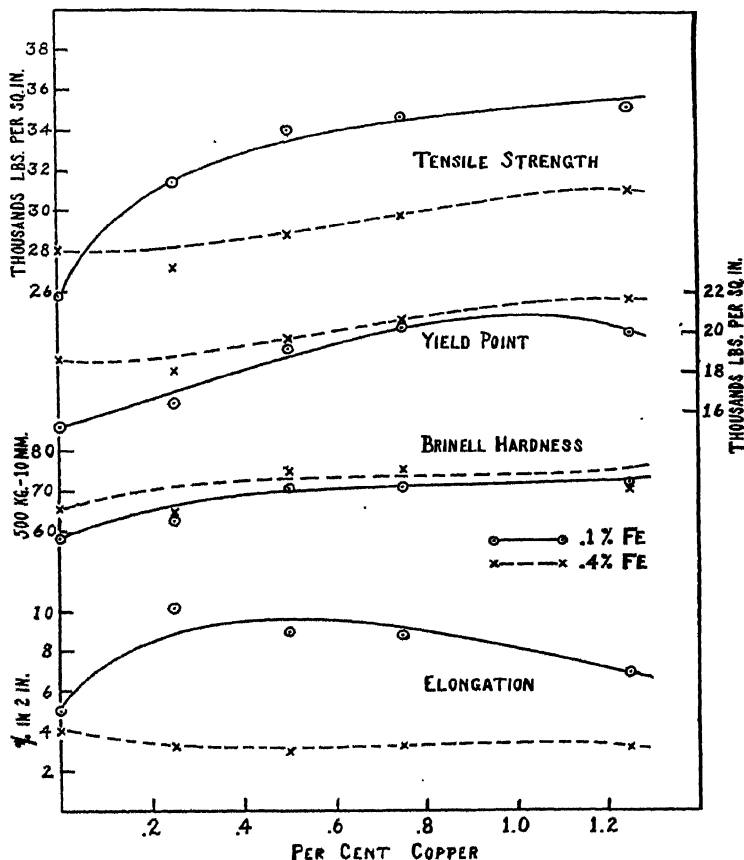
FIG. 6.—EFFECT OF COPPER ON MECHANICAL PROPERTIES OF SOME SAND-CAST HEAT-TREATED ALLOYS CONTAINING ABOUT 5 PER CENT. SILICON, 0.35 PER CENT. MAGNESIUM.
    Quenched from 20 hr. at 1000° F.; aged four days at room temperature prior to testing.

sidered to be average values obtainable on compositions within these ranges under good casting conditions.   The yield point, tensile strength and Brinell hardness increase continuously with magnesium content while the elongation either decreases continuously, as in the higher silicon alloys, or remains practically constant as with the 5 per cent. silicon alloys.   The yield point, tensile strength and Brinell hardness are increased

as the silicon content increases. The elongations of the 10 and 13 per cent. silicon alloys are higher at the lower magnesium contents than that of the 5 per cent. silicon alloy, but the elongation of the latter remains practically constant while this property in higher silicon alloys decreases continuously.
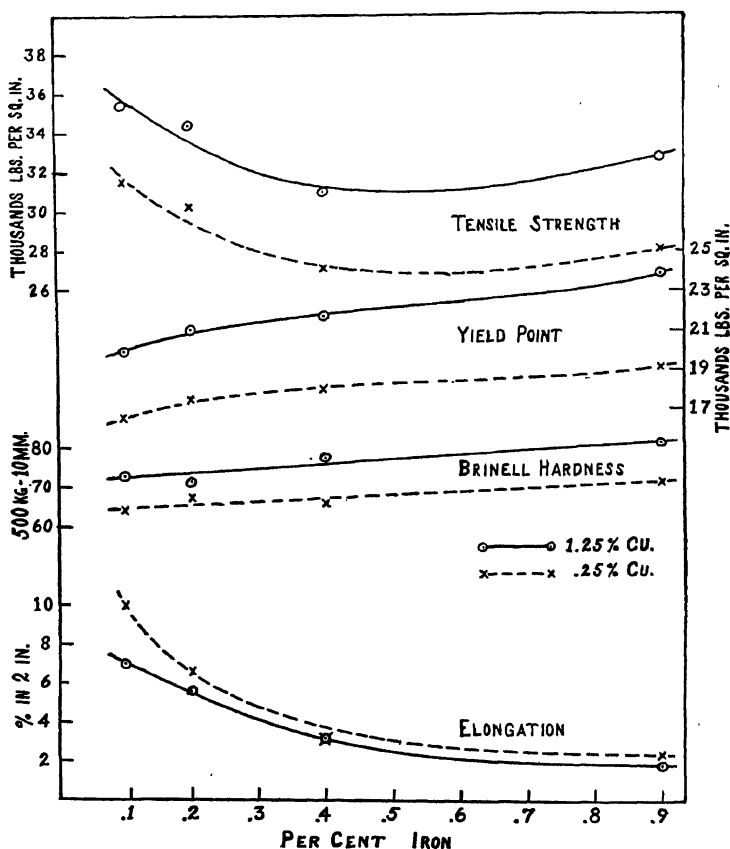
FIG. 7.—EFFECT OF IRON ON MECHANICAL PROPERTIES OF SOME SAND-CAST HEAT-TREATED ALLOYS CONTAINING ABOUT 5 PER CENT. SILICON, 0.35 PER CENT. MAGNESIUM. Quenched from 20 hr. at 1000° F.; aged four days at room temperature prior to testing.

Fig. 3 indicates the effect of a precipitation heat treatment on the mechanical properties of the alloys just described. Yield point, tensile strength and Brinell hardness are increased at the expense of elongation.

Fig. 4 and Table 7 give data on the mechanical properties of some heat-treated sand-cast alloys containing 5, 7, 9 and 11 per cent. of silicon, with various magnesium contents. Here, as in the chill-cast alloys,

yield point, tensile strength and hardness increase while elongation decreases with increasing silicon or magnesium contents.

Silicon.—The curves of Fig. 5, taken from the data of Tables 9, 10 and 11, illustrate the variation in mechanical properties with silicon content of heat-treated alloys containing about 0.3 per cent. magnesium,
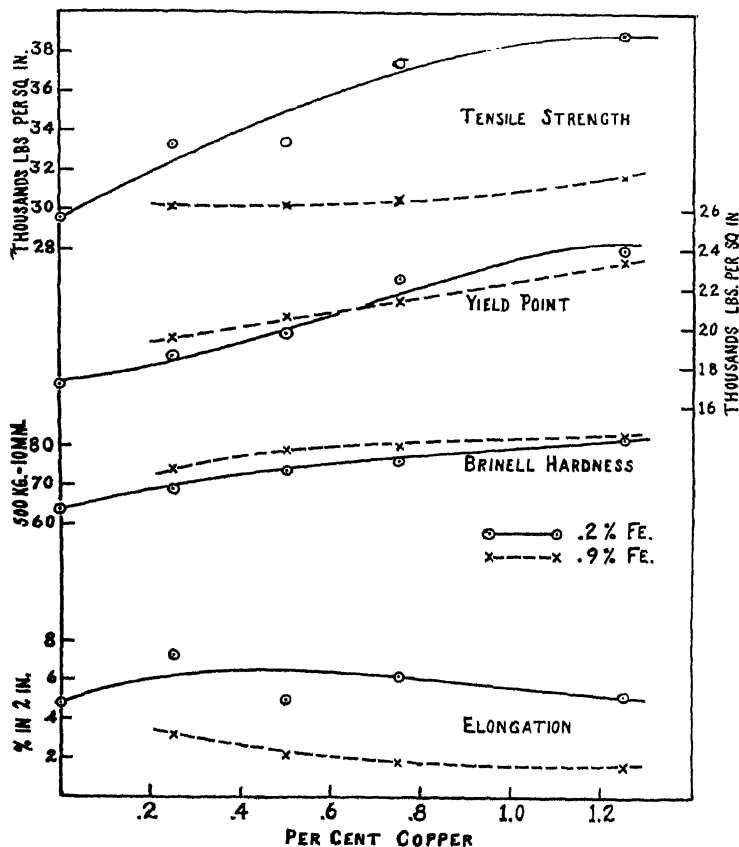
FIG. 8.—EFFECT OF COPPER ON MECHANICAL PROPERTIES OF SOME SAND-CAST HEAT-TREATED ALLOYS CONTAINING ABOUT 7.5 PER CENT. SILICON, 0.35 PER CENT. MAGNESIUM.

Quenched from 20 hr. at 1000° F.; aged four days at room temperature prior to testing.

0.2 per cent. iron, 0.05 per cent. and 0.75 per cent. copper. Tensile strength increases rapidly with silicon content; yield strength and Brinell hardness increase more slowly. Elongation decreases rapidly up to about 5 per cent. silicon, then is practically constant to about 10 per cent. silicon.

Copper.—The elongations of the higher copper alloys (Fig. 5) are generally slightly higher than those of the corresponding low-copper

alloys. An explanation of this rather unexpected result may be the smaller grain size of the higher copper alloys.

The curves of Figs. 6, 7, 8 and 9, taken from the data of Tables 9 and 10, illustrate the general effect of copper on the mechanical properties
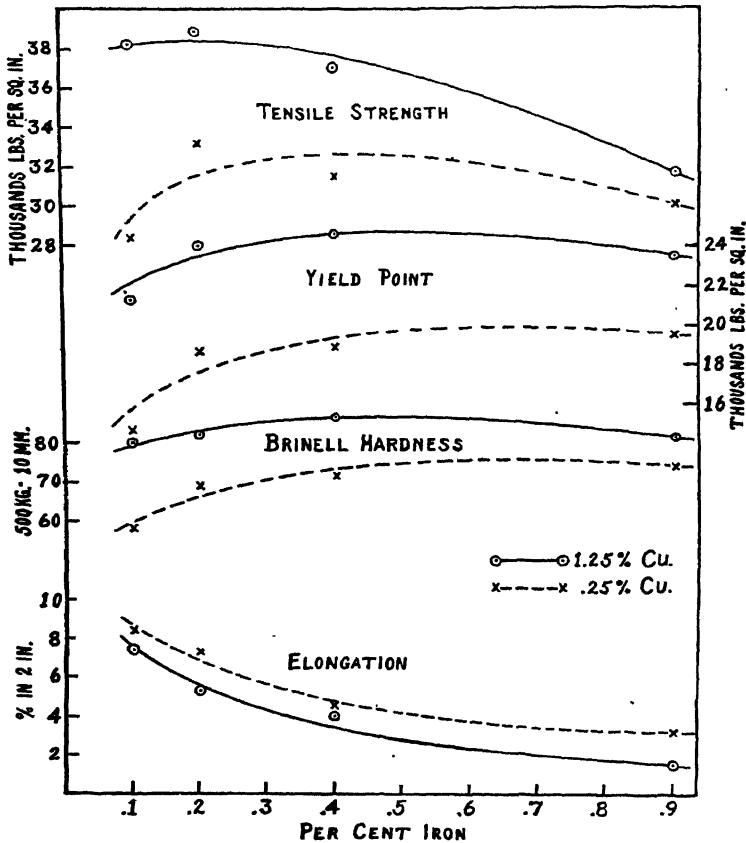
FIG. 9.—EFFECT OF IRON ON MECHANICAL PROPERTIES OF SOME SAND-CAST HEAT-TREATED ALLOYS CONTAINING ABOUT 7.5 PER CENT. SILICON, 0.35 PER CENT. MAGNESIUM.

Quenched from 20 hr. at 1000° F.; aged four days at room temperature prior to testing.

of some heat-treated aluminum-silicon-magnesium alloys containing 5 and 7.5 per cent. silicon and 0.35 per cent. magnesium. Increasing amounts of copper markedly increase the tensile strength and are somewhat less effective in increasing the yield strength and Brinell hardness. The elongation increases with the copper content to about 0.4 or 0.5 per cent. copper and then decreases slowly.

Iron.—Figs. 6, 7, 8 and 9 also illustrate that the general effect of increasing iron concentrations is to decrease tensile strength and elongation. Yield strength and Brinell hardness are increased slightly.

TABLE 7.—*Mechanical Properties of Some Normal · Heat-treated Al-Si and Al-Si-Mg Alloys[a]*

Cast at 1250° F. in Green-sand Molds; Heat-treated 20 Hr. at 1025° F., Quenched in Water, Aged Three Days at Room Temperature

Sample	Percentage Composition						Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 1000 Kg., 10 Mm., 10 Sec.
	By Mixture		By Analysis						
	Si	Mg	Cu	Fe	Si	Mg			
6334	5.0	0.0		0.39	5.05	0.0	19,060	10.5	37.4
6335	5.0	0.1		0.40	4.94	0.17	21,180	8.8	46.4
6336	5.0	0.2		0.40	4.94	0.26	24,680	6.6	54.6
6337	5.0	0.3	0.05	0.39	5.04	0.30	30,100	8.0	63.5
6342	7.0	0.0	0.05	0.43	6.92	0.0	20,900	9.5	43.1
6343	7.0	0.1	0.06	0.43	6.82	0.09	22,390	7.0	50.6
6344	7.0	0.2	0.05	0.41	6.92	0.27	25,690	5.0	60.7
6345	7.0	0.3	0.05	0.41	6.88	0.31	30,230	5.8	67.8
6349	9.0	0.0	0.05	0.40	9.22	0.0	22,510	8.6	48.2
6350	9.0	0.1	0.06	0.41	8.79		24,820	6.5	54.9
6351	9.0	0.2		0.46	8.99		27,180	5.0	65.0
6352	9.0	0.3	0.05	0.39	8.98	0.37	28,400	3.5	68.9
6356	11.0	0.0	0.10	0.46	11.03	0.0	21,940	5.0	51.1
6357	11.0	0.1		0.50	10.62	0.10	23,460	4.0	57.0
6358	11.0	0.2		0.51	10.42	0.26	26,240	2.8	58.8
6359	11.0	0.3		0.52	10.95	0.36	28,720	3.1	73.9

[a] Each value the average of four tests.

MODIFICATION

The properties of sand-cast heat-treated aluminum-silicon-magnesium alloys can be materially altered by applying the process of modification[7] prior to casting. This process, as ordinarily carried out, consists in the addition of a small amount of metallic sodium or of a sodium-producing compound to the molten metal just before casting. A marked refinement of the silicon particles results from such treatment, and the casting so produced responds to heat treatment more quickly and with a somewhat different combination of properties than is obtained with "normal

[7] R. S. Archer and L. W. Kempf: *Op. cit.*
    A. Pacz: U. S. Patent 1387900. Applied for February 13, 1920; issued August 16, 1921.
    J. D. Edwards, F. C. Frary and H. V. Churchill: U. S. Patent 1410461. Applied for Nov. 27, 1920; issued March 1, 1922.

TABLE 8.—*Chemical Composition of Alloys*

| Sample | Percentage Composition | | | | | | | | Percentage of Aluminum in Ingot Used |
| | By Mixture | | | | By Analysis | | | | |
	Cu	Fe	Si	Mg	Cu	Fe	Si	Mg	
7119	0.0	0.1	5.0	0.3	0.02	0.17	4.97	0.38	99.85
7265	0.25	0.1	5.0	0.3	0.25		4.78	0.35	99.85
7301	0.50	0.1	5.0	0.3	0.50	0.15	4.89	0.39	99.85
7299	0.75	0.1	5.0	0.3	0.72		4.82	0.36	99.85
7205	1.25	0.1	5.0	0.3	1.25	0.17	4.64	0.32	99.85
7122	0.0	0.2	5.0	0.3	0.028	0.25	4.98	0.36	99.70
7222	0.25	0.2	5.0	0.3	0.25		4.50	0.38	99.70
7223	0.50	0.2	5.0	0.3	0.51		4.60	0.37	99.70
7208	0.75	0.2	5.0	0.3	0.71	0.20	4.83	0.37	99.70
7209	1.25	0.2	5.0	0.3	1.27	0.20	4.75	0.39	99.70
7125	0.0	0.4	5.0	0.3			4.86	0.39	99.2
7226	0.25	0.4	5.0	0.3	0.25		4.59	0.38	99.2
7227	0.50	0.4	5.0	0.3	0.47		4.72	0.39	99.2
7212	0.75	0.4	5.0	0.3	0.75	0.47	4.70	0.37	99.2
7213	1.25	0.4	5.0	0.3	1.21		4.54	0.38	99.2
7263	0.25	0.9	5.0	0.3		1.12		0.35	99.2
7264	0.50	0.9	5.0	0.3	0.53	1.0	4.60	0.32	99.2
7257	0.75	0.9	5.0	0.3	0.73	0.92	4.51	0.32	99.2
7258	1.25	0.9	5.0	0.3	1.20	0.92	4.58	0.36	99.2
7120	0.0	0.1	7.5	0.3	0.023	0.17	7.3	0.30	99.85
7216	0.50	0.1	7.5	0.3	0.51	0.16	6.76	0.35	99.85
7206	0.75	0.1	7.5	0.3	0.77	0.16	7.04		99.85
7207	1.25	0.1	7.5	0.3	1.26	0.14	7.18	0.30	99.85
7123	0.0	0.2	7.5	0.3			7.60	0.38	99.70
7221	0.25	0.2	7.5	0.3	0.23	0.17	7.27	0.36	99.70
7220	0.50	0.2	7.5	0.3	0.51	0.19	7.31	0.34	99.70
7210	0.75	0.2	7.5	0.3	0.76		7.18	0.38	99.70
7211	1.25	0.2	7.5	0.3	1.27	0.24	7.39	0.38	99.70
7126	0.0	0.4	7.5	0.3	0.075	0.37	7.53	0.38	99.2
7225	0.25	0.4	7.5	0.3	0.22	0.41	6.92	0.36	99.2
7224	0.50	0.4	7.5	0.3	0.44	0.45	7.06	0.37	99.2
7214	0.75	0.4	7.5	0.3	0.76		6.92	0.36	99.2
7215	1.25	0.4	7.5	0.3	1.25		7.36	0.35	99.2
7262	0.25	0.9	7.5	0.3	0.34	1.05		0.36	99.2
7261	0.50	0.9	7.5	0.3	0.50	0.89	7.01	0.32	99.2
7259	0.75	0.9	7.5	0.3	0.69	0.89	7.20	0.31	99.2
7260	1.25	0.9	7.5	0.3	1.26	0.88	7.14	0.32	99.2
7296	0.0	0.2	3.5	0.3	0.04		3.68	0.35	99.70
7297	0.75	0.2	3.5	0.25	0.77		3.43	0.29	99.70
7298	0.25	0.2	7.5	0.2	0.25		7.59	0.24	99.70
7219	0.50	0.2	3.5	0.3	0.45		3.96	0.31	99.85

TABLE 9.—*Effect of Copper and Iron on the Mechanical Properties of a Sand-cast Alloy Containing About 5 Per Cent. Silicon and 0.35 Per Cent. Magnesium*

Compositions Are Tabulated in Table 8. Values Are the Average of Six Tests Except Where Obviously Defective Bars Were Discarded. All Bars Aged Four Days at Room Temperature Prior to Testing

Sample	As Cast				20 Hr. at 1000° F., Quenched				20 Hr. at 1025° F., Quenched			
	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.
7119	12,210	18,110	2.2	50.6	15,170	25,810	5.0	58.4	15,440	25,660	5.5	59.7
7265	12,390	22,040	4.0	51.7	16,420	31,530	10.1	64.0	17,110	32,900	13.2	63.0
7301	13,610	23,350	3.6	55.3	19,330	34,170	9.0	71.0	18,320	32,350	9.0	68.7
7299	14,280	24,040	3.7	56.2	20,270	34,670	8.9	71.4	19,370	33,270	8.0	71.5
7205	15,740	23,710	2.2	56.3	19,910	35,290	7.0	73.3				
7122	12,490	20,540	3.2	50.3	14,680	25,480	5.1	58.6	16,150	29,310	8.3	60.7
7222	12,610	20,920	3.3	49.8	17,420	30,260	6.6	67.7	18,140	32,860	9.1	69.1
7223	14,120	21,500	2.5	54.0	18,280	30,820	6.0	67.7	18,470	31,610	7.4	69.3
7208	15,300	21,070	1.8	60.4	20,390	32,100	4.8	71.8	20,080	31,390	5.3	76.0
7209	16,430	23,790	2.0	61.0	21,130	34,310	5.7	71.0				
7125	15,590	20,720	1.5	54.9	18,640	28,080	4.0	65.5	19,150	28,170	3.5	67.7
7226	13,690	20,490	2.0	53.5	18,010	27,060	3.2	65.4	18,780	27,980	4.0	67.7
7227	16,040	20,990	1.3	60.0	19,740	28,940	3.0	74.6	20,150	28,390	3.5	75.0
7212	16,650	22,130	1.5	59.0	20,470	29,800	3.3	75.7	20,680	28,410	3.0	76.0
7213	16,860	23,860	1.5	63.0	21,620	31,060	3.2	71.7				
7263	15,340	23,030	1.5	61.8	18,990	28,060	2.2	71.5	19,170	28,210	3.2	71.2
7264	17,460	24,120	1.5	65.7	20,470	28,850	2.2	75.1	20,150	30,200	3.4	68.6
7257	15,550	23,830	2.0	62.5	19,250	29,290	2.5	72.7				
7258	18,850	26,190	1.0	65.5	23,820	32,660	2.0	81.0				

TABLE 10.—*Effect of Copper and Iron on the Mechanical Properties of a Sand-cast Alloy Containing About 7.5 Per Cent. Silicon and 0.35 Per Cent. Magnesium*

Compositions Are Tabulated in Table 8. Values Are the Average of Six Tests Except Where Obviously Defective Bars Were Discarded. All Bars Aged Four Days at Room Temperature Prior to Testing

Sample	As Cast				20 Hr. at 1000° F., Quenched				20 Hr. at 1025° F., Quenched			
	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.
7120	14,230	23,400	3.0	56.1	16,810	31,480	7.1	63.5	19,320	33,850	7.0	71.5
7216	14,540	22,770	2.5	53.5	19,500	33,940	5.8	74.7	19,690	32,900	5.9	73.8
7206	15,610	24,410	2.8	58.9	17,610	33,770	7.3	71.8				
7207	16,270	25,410	2.4	59.3	21,230	38,160	7.4	80.2				
7123	13,690	22,080	2.8	54.3	17,140	29,630	4.8	64.4	18,250	33,390	7.0	68.0
7221	14,710	22,550	2.4	54.9	18,620	33,260	7.3	69.6	19,080	35,080	9.1	69.5
7220	14,320	21,720	2.2	55.2	19,870	33,350	5.0	74.6		34,100	7.5	70.0
7210	17,480	25,550	2.0	61.2	22,610	37,490	6.2	76.3				
7211	17,290	25,520	2.0	65.8	23,980	38,840	5.3	82.0		10,000	0.0	58.0 Burnt
7126	15,560	22,560	1.5	57.9	19,340	30,470	3.7	71.0	19,620	30,980	4.6	71.5
7225	15,410	22,970	1.7	58.2	18,840	31,510	4.4	71.4				
7224	15,420	22,540	1.5	56.6	20,320	32,360	3.8	73.3	20,390	33,500	5.5	77.1
7214	17,160	25,200	1.0	62.9	19,850	33,590	3.7	77.1				
7215	18,640	26,410	1.7	67.2	24,650	37,020	4.0	86.7		10,000	0.0	61.5 Burnt
7262	16,750	25,320	1.5	65.0	19,520	30,070	3.2	74.3	19,410	30,280	3.6	73.5
7261	17,380	24,000	1.3	65.3	20,570	30,040	2.1	79.0	20,680	29,860	3.0	74.3
7259	17,350	25,790	1.0	65.9	21,400	30,710	1.8	79.4				
7260	18,670	26,430	1.0	67.7	23,500	31,760	1.6	81.4				

TABLE 11.—*Mechanical Properties of Some Miscellaneous Al-Si-Mg and Al-Si-Mg-Cu Alloys*
Chemical Compositions Are Tabulated in Table 8. Each Value the Average of Six Tests Except Where Obviously Defective Bars Were Discarded. All Bars Aged Four Days Prior to Testing

Sample	As Cast				20 Hr. at 1000° F., Quenched				20 Hr. at 1025° F., Quenched			
	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.
7296	11,380	18,730	3.3	49.1	15,290	24,430	8.8	59.3	14,960	27,700	10.0	56.9
7297	12,430	22,420	4.5	52.4	17,240	31,880	10.5	64.2	16,520	32,520	12.1	61.9
7298	13,370	22,660	3.3	53.2	15,550	30,490	8.0	64.2	15,940	30,730	9.4	62.3
7219	14,350	21,830	3.0	53.6	17,750	30,065	6.8	65.3	18,340	31,320	7.7	68.7

alloys." With a given composition and heat treatment, a modified alloy is usually more ductile and softer than the same alloy in the normal or unmodified state. Modification may thus be utilized to shorten the time of heat treatment, or to permit the use of compositions (with high silicon and high iron) not suitable in the normal condition when high ductility is required.

Table 12 gives some data on the mechanical properties of three modified and heat-treated alloys containing various amounts of copper, iron and magnesium. The general relationships between mechanical properties and chemical compositions of the normal alloys also hold true with the modified alloys. The elongation is usually appreciably higher.

The attainment of maximum tensile properties in the binary aluminum-silicon alloys by means of modification entails very careful control of all the factors entering into the process. Because of the subsequent heat treatment, the modification of aluminum-silicon-magnesium alloys is not such a critical process. The amount of sodium added, the holding time and the composition may vary over relatively wide limits without greatly affecting the tensile properties.

EFFECT OF POURING TEMPERATURE

In the production of miscellaneous commercial castings it is sometimes necessary to pour the molten metal at temperatures other than the optimum for maximum tensile properties. Some alloys are more affected by variations in pouring temperatures than others. Table 13 gives the tensile properties of test bars of an aluminum-silicon-magnesium alloy when cast at 1250° F., 1350° F. and 1450° F. Included in the table are tests representative of the effect of pouring temperature on the properties of a heat-treated 4 per cent. copper alloy. The aluminum-silicon alloy is considerably less affected by elevated casting temperatures than the aluminum-copper alloy.

This table also illustrates the general effect of duration of the solution treatment on the properties of sand castings. Elongation increases while tensile strength and Brinell hardness decrease with increase in time at the solution temperature. The properties of sample 5411, Table 13, were obtained with partly modified material and may be compared with the properties of sample 6358, Table 7, and sample 5154, Table 14, examples of similar alloys in the normal and completely modified conditions respectively.

MICROSTRUCTURE

Figs. 10 to 19 illustrate structures typical of the normal sand-cast aluminum-silicon-magnesium-copper alloys. The dark gray constituent occurring in greatest abundance is silicon. The white matrix is the aluminum-rich solid solution. The small black particles such as appear

TABLE 12.—*Properties of Modified and Heat-treated Aluminum-silicon-magnesium Alloys* Modified with 0.05 Per Cent. Sodium, Cast in Green-sand Test-bar Molds at 1225° F. and Heat-treated As Shown

	Cu	Fe	Mg	Si
Sample 5041:	0.09	0.69	0.19	9.34
Sample 5045:	0.18	0.34	0.27	9.76
Sample 5046:	0.11	0.47	0.16	9.86

Heat Treatment[a]	Sample 5041				Sample 5045				Sample 5046			
	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 1,000 Kg., 10 Mm.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 1,000 Kg., 10 Mm.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 1000 Kg., 10 Mm.
995° F., 14 hr.	13,946	28,542	13.4	54.5	16,712	31,376	7.0	65.8	13,643	28,555	12.2	56.1
995° F., 20 hr.	14,038	28,316	10.3	55.3	17,433	31,496	7.5	67.8	14,130	29,503	12.2	57.3
995° F., 45 hr.	14,032	27,831	10.2	56.3	17,406	31,762	8.6	96.6	13,816	28,841	13.3	58.0
1022° F., 14 hr.	14,236	29,366	9.5	57.3	17,850	32,100	7.3	72.2	14,144	30,737	14.0	58.9
1022° F., 20 hr.	15,527	30,947	13.4	60.1	18,100	32,455	7.3	72.2	15,514	31,231	13.1	62.0
1022° F., 45 hr.	14,773	30,488	13.2	61.0	18,112	31,913	7.5	74.0	15,132	31,186	13.5	63.2
1049° F., 14 hr.	15,150	31,200	16.0	59.6	17,783	33,020	9.2	72.4	14,192	30,956	14.4	59.8
1049° F., 20 hr.	15,600[b]	31,350[b]	13.0[b]	60.8	17,853	32,325	7.0	71.5	14,983	31,392	15.3	61.8
1049° F., 45 hr.	15,025	30,325	13.5	59.8	17,859	32,394	8.9	74.3	15,228	30,918	13.9	62.8

[a] All bars quenched in water and aged two days at room temperature before testing.

[b] These values are from a single test bar. All other values given are averages of at least three tests. When bad defects, such as dross, appeared in the fractures, the results of the test were not included in calculating the average.
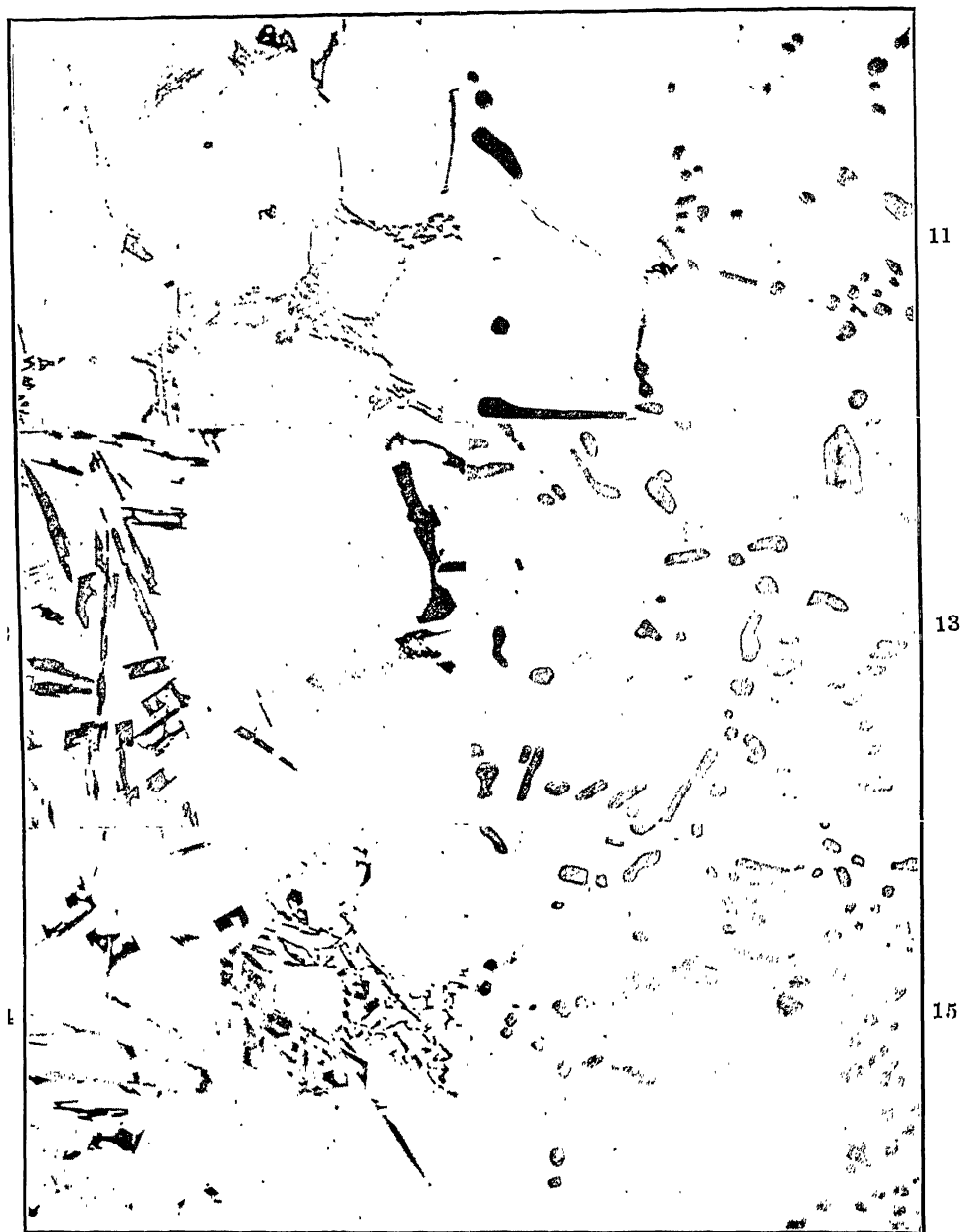
FIG. 10.—SAND-CAST ALLOY CONTAINING 3.5 PER CENT. SILICON, 0.25 PER CENT.
    MAGNESIUM, 0.75 PER CENT. COPPER, 0.2 PER CENT. IRON.   X 400.   UNETCHED.
FIG. 11.—SAME ALLOY AS FIG. 10.   HEAT-TREATED 20 HR. AT 1000° F., QUENCHED.
                    X 400.   UNETCHED.
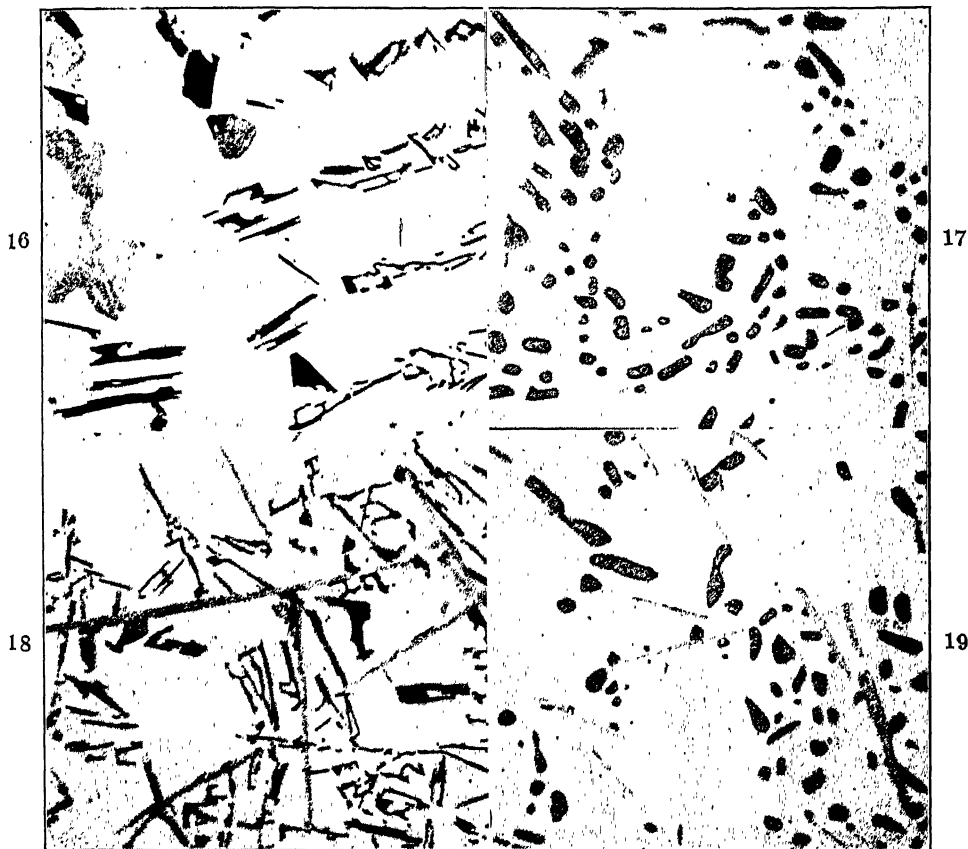
FIG. 16.—SAND-CAST ALLOY CONTAINING 7.5 PER CENT. SILICON, 0.75 PER CENT
   COPPER, 0.3 PER CENT. MAGNESIUM, 0.2 PER CENT. IRON.   UNETCHED.
FIG. 17.—SAME ALLOY AS FIG. 16.   HEAT-TREATED 20 HR. AT 1000° F., QUENCHED.
   UNETCHED.
FIG. 18.—SAND-CAST ALLOY CONTAINING 7.5 PER CENT. SILICON, 0.75 PER CENT.
   COPPER, 0.3 PER CENT. MAGNESIUM, 0.9 PER CENT. IRON.   UNETCHED.
FIG. 19.—SAME ALLOY AS FIG. 18.   HEAT-TREATED 20 HR. AT 1000° F., QUENCHED.
   UNETCHED.
   All × 400.

FIG. 12.—SAND-CAST ALLOY CONTAINING 5 PER CENT. SILICON, 0.3 PER CENT. MAG-
   NESIUM, 0.75 PER CENT. COPPER, 0.2 PER CENT. IRON.
   Etched with 0.5 per cent. hydrofluoric acid.
FIG. 13.—SAME ALLOY AS FIG. 12.   HEAT-TREATED 20 HR. AT 1000° F., QUENCHED.
   Etched with 0.5 per cent. hydrofluoric acid.
FIG. 14.—SAND-CAST ALLOY CONTAINING 5 PER CENT. SILICON, 0.75 PER CENT. COPPER,
   0.3 PER CENT. MAGNESIUM, 0.9 PER CENT. IRON.   UNETCHED.
FIG. 15.—SAME ALLOY AS FIG. 14.   HEAT-TREATED 20 HR. AT 1000° F., QUENCHED.
   UNETCHED.
   All × 400.

near the top middle portion of Fig. 10 and scattered along the light gray needle near the left-hand portion of Fig. 18 are Mg_2Si. The chunky half-tone particles are the copper-bearing constituent, which may contain some iron and silicon as well as aluminum. It is a little difficult to distinguish the copper constituent from $\beta(Fe-Si)$, which is also light gray but slightly darker than the copper constituent. The $\beta(Fe-Si)$, however, is characteristically needlelike while the copper constituent is usually more chunky or filigree-like. A few particles of copper constituent occur along the iron-bearing needles of Fig. 18 where the slight difference in tone of the two is recognizable. By comparing the structures of the as-cast and heat-treated alloys it may be noted that most of the half-tone constituent in the low-iron alloys is due to the copper, inasmuch as it disappears on heat treatment. A few small particles of iron constituent are left scattered about between the silicon particles.

TABLE 13.—*Effect of Pouring Temperature on Mechanical Properties of Sand-cast Alloys*[a]

Sample	Percentage Composition				Tensile Strength, Lbs. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 1000 Kg., 10 Mm., 30 Sec.	Pouring Temperature	Heat Treatment
	Cu	Fe	Si	Mg					
5411	0.05	0.15	11.68	0.17	29,350	6.0	67.3	1450° F.	2 hr. 1025° F. Quenched, aged four days at room temperature.
					30,240	6.7	68.6	1350° F.	
					31,650	7.5	68.2	1250° F.	
					27,710	10.7	56.8	1450° F.	20 hr. at 1025° F. Quenched, aged four days at room temperature.
					28,290	11.2	56.1	1350° F.	
					30,340	9.5	56.1	1250° F.	
4765	4.34	0.69	0.76	0.0	26,880	6.4	65.9	1400° F.	12 hr. at 960° F. Quenched, aged four days at room temperature.
4764					30,700	6.2	72.5	1350° F.	
4762					33,010	9.1	67.2	1250° F.	

[a] Each value the average of three tests.

The heat-treated alloys generally show only spheroidized silicon and the iron constituent in a matrix of aluminum-rich solid solution. The higher tensile strength and elongation of the heat-treated alloys is quite compatible with solution of the Mg_2Si, the copper constituent, and perhaps some of the silicon. The marked spheroidizing of the silicon favors higher elongations. The needlelike or platelike form of the $\beta(Fe-Si)$ undoubtedly forms planes of weakness in the higher iron alloys.

In the as-cast specimens the silicon particles are generally smaller in the low-silicon alloys, which may be due to the chilling effect of the relatively larger volume of aluminum-rich dendrites, which crystallize from the melt before the freezing of aluminum-silicon eutectic.

CASTING QUALITIES

The excellent casting characteristics of the aluminum-silicon alloys seem to be largely retained in the alloys here under discussion, which contain small amounts of magnesium and perhaps copper, in addition to the silicon. Fluidity and freedom from hot shortness become apparent with 3 per cent. silicon or less and increase up to approximately eutectic composition (11 to 14 per cent. silicon, depending on whether the alloy is normal or modified). At or near the eutectic composition, however, there is a tendency toward internal shrinkage, which necessitates careful feeding and a high ratio of risers to castings. The feeding characteristics of the alloys are better at intermediate silicon contents, the alloy containing 5 per cent. silicon, for example, being better in this respect than the 10 per cent. or 13 per cent. silicon alloys. It is to be expected that the alloys containing less than about 1 per cent. magnesium plus copper in addition to the silicon will have casting properties comparable with those of binary aluminum-silicon alloys of the same silicon content, although some differences in details may be found.

The small amount of sodium introduced in the modified aluminum-silicon alloys results in a more rapid formation of oxide film on the surface of the molten metal and also apparently in a film of greater toughness. In some foundries it is felt that there is a greater tendency for these films to be trapped in castings with the possibility of causing misruns, cold shuts, leaks or other foundry defects. These difficulties can be overcome and good castings are being made of modified silicon alloys. Nevertheless, some may prefer a low silicon content without modification to a high silicon content with modification. It will be recalled that in the heat-treated condition the tensile properties of the low-silicon alloys containing small amounts of magnesium, with or without copper, and with low iron content, are similar to those of the higher silicon alloys of this type which have been modified with sodium and heat-treated.

One of the most valuable practical advantages of these alloys is their ability to produce castings free from leaks. This advantage seems to obtain in general over the range of silicon under consideration here (3 to 12 per cent.), subject to the considerations just discussed in connection with modification.

These remarks on casting qualities are general in nature and of less value than the results of extended commercial experience with one or more specific alloy compositions. Such experience is lacking, but commercial castings of various types have been made with results that are interesting. One case was that of a casting weighing several hundred pounds, which, because of cracking, was difficult to produce in a 4 per cent. copper alloy. This piece was readily cast from an alloy containing 10 per cent. silicon and 0.2 per cent. magnesium, modified with sodium. Cylinder heads for water-cooled internal-combustion motors are intricate

castings with many changes in section thickness and much complicated core work. One of the requirements is that the finished casting be leak-proof under hydraulic pressure. It has been found much easier to obtain substantially leak-proof castings from an alloy containing 5 per cent. silicon, 0.4 per cent. magnesium and 0.75 per cent. copper than from Y alloy or 195 alloy.

CORROSION RESISTANCE

Service and laboratory tests have shown the aluminum-silicon alloys to be generally superior to the aluminum-copper or aluminum-copper-zinc casting alloys in respect to resistance to weathering and salt-water corrosion. The results of some salt-spray corrosion tests given in Table 14 permit a comparison of two examples of the aluminum-silicon-magnesium alloys here under discussion with the commonly used 5 and 13 per cent. silicon alloys, and also an aluminum-copper alloy. The specimens used in these tests were made under similar conditions, cast in green sand in the form of $\frac{1}{2}$ in. dia. test bars, machined to approximately 0.475 in. dia., and subjected to the spray of a 20 per cent. sodium chloride solution for one year. The control specimens which were machined to the same size and tested at the same time as the corroded bars were protected with a coating of paraffin wax and stored at room temperature in the laboratory for the duration of the corrosion period.

With sample 5154, conditions were especially favorable to high resistance to corrosion in that the iron content was fairly low and the bars had no precipitation heat treatment. This material showed higher resistance to corrosion than any of the standard alloys included in the table. In the case of sample 5153, it is considered that both the higher iron content and the precipitation heat treatment were unfavorable but in spite of these factors this material compares fairly well with those listed above it in Table 14.

Appearance is often an important criterion in appraising resistance to corrosion. After attack by salt spray the aluminum-silicon and aluminum-silicon-magnesium alloys of Table 14 were similar in appearance, having in general a light gray color as compared with a considerably darker color in the case of the aluminum-copper alloy.

Some of the best mechanical properties reported in this paper were obtained with alloys containing about 0.25 to 1.25 per cent. copper in addition to silicon and magnesium. In the absence of actual corrosion test results it may be of interest to consider the probable effect of such an amount of copper. In the heat-treated condition substantially all of this copper is in solid solution, and because of the low copper content it seems probable that little if any precipitation of $CuAl_2$ will take place during aging at ordinary temperatures. It seems likely, therefore, that the presence of this copper in the heat-treated alloys will not greatly

TABLE 14.—Effect of Salt-spray Corrosion for One Year on the Tensile Properties of Some Sand-cast Aluminum Alloys

Sample	Uncorroded Blanks				Corroded Specimens				Percentage Change		Percentage Composition				Condition
	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	Tensile Strength	Elongation	Cu	Fe	Si	Mg	
5152	27,370	36,180	4.0	80.9	22,390	29,260	2.2	85.7	−19.1	−45.0	4.57	0.76	0.85	0.0	Heated 12 hr. at 960° F., quenched.
5686	11,350	21,460	4.1	54.9	10,660	18,760	2.8	53.7	−12.5	−33.0	0.4	0.6	5.0	0.0	As cast.
5129	14,470	29,030	11.2	55.6	14,140	26,100	5.6	57.9	−10.1	−50.0	0.19	0.29	13.49	0.0	Modified with 0.08 per cent. sodium.
5153	16,350	25,550	10.2	57.5	16,530	26,440	4.6	62.1	− 7.4	−55.0	0.09	0.69	9.34	0.19	Heated 2 hr. at 1025° F., quenched, aged 16 hr. at 310°F.
5154	15,830	33,270	18.7	60.3	15,260	32,490	14.2	64.2	− 2.4	−24.0	0.0	0.14	10.15	0.18	Heated 2 hr. at 1025° F. quenched.

alter the effect of corrosion on physical properties, although it may cause a greater darkening of the surface.

MACHINABILITY

The binary aluminum-silicon alloys do not machine as easily as the aluminum-copper alloys. The chief difficulties are dragging, which is due to the plasticity of the material, and increased wear on cutting tools, which is due to the abrasive nature of the silicon. The heat-treated aluminum-silicon-magnesium alloys machine more easily. The plasticity of the matrix is decreased, so that there is little trouble from dragging. There may be somewhat more tool wear, especially with the higher silicon contents, than with the aluminum-copper alloys. Machining is commercial with steel tools and tool wear can be reduced to a minimum by the use of tungsten carbide tools. This tool material has been in satisfactory use for some time in machining a much harder high-silicon piston alloy. Crank-case and cylinder-head castings of the aluminum-silicon-magnesium alloys under discussion here have been satisfactorily machined by using the tool set-ups ordinarily employed in machining the same castings in aluminum-copper alloys.

SOME PROPERTIES OF CASTINGS

Strength.—It is generally recognized that the properties of test specimens cut from commercial castings are apt to be somewhat lower than those of separately cast bars. A casting is generally considered good when specimens cut from it have 75 to 80 per cent. of the strength of separately cast test specimens. In Table 15 are given the results of some tests on bars cut from castings and also on separately cast bars of three different alloys. The high ratio of strength in the casting to strength of the separately cast bars in the aluminum-silicon-magnesium alloys is consistent with the excellent casting qualities of these alloys.

Specific Gravity.—The addition of silicon and magnesium to aluminum, unlike the addition of most other common alloying metals, decreases its specific gravity, the specific gravity of silicon being 2.4 and of magnesium 1.7. The specific gravities of castings of the alloys described in this paper will vary from about 2.65 to 2.70, depending on the chemical composition and manner of casting. This is about 6.5 per cent. lighter than No. 112 alloy and about 4 per cent. lighter than 195 alloy.

Fatigue Resistance.—In some applications of castings the resistance of the material to repeated stresses or fatigue may be important. The maximum stress that aluminum alloys will endure without failure decreases as the number of stress cycles increases. In the extensive investigations in the Research Laboratories of the Aluminum Co. of America, under the direction of R. L. Templin, the stress at 500,000,000 cycles has been found an adequate criterion of endurance limit. On

TABLE 15.—*Strength in Castings of Various Alloys*

	Test Bars Cut from Castings		Separately Cast Test Bars		Ratio of Tensile Strength of Casting to Tensile Strength of Test Bars	Chemical Composition					Heat Treatment
	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.		Cu	Fe	Si	Mg	Ni	
1. Al-Si-Mg alloy outrigger casting......	26,800	6.3	28,890	8.3	0.93	0.3	10.0	0.2	0.0		12 hr. at 1025° F., quenched.
2. Cylinder-head casting 168* alloy......	28,430	0.9	45,540	1.0	0.62	3.5	1.2	0.8	0.5	0.7	5 hr. at 980° F., quenched, 10 hr. at 340° F.
3. Cylinder-head casting Al-Si-Mg alloy..	28,570	2.5	27,470	5.5	1.04	0.75	0.3	5.0	0.4	0.0	16 hr. at 1000° F., quenched, 2 hr. at 550° F.

* Alloy X.   For description see A. J. Lyons: Alloys for Aircraft Engine Pistons and Cylinder Heads.   4th Natl. Aeronautic Meeting, May 19, 1930, Auspices A. S. M. E.

this basis the endurance limit of 43 alloy (5 per cent. silicon) is around 6500 lb. per sq. in. and that of 47 alloy (13 per cent. silicon, modified) is about 6000 lb. per sq. in.   The endurance limit of an alloy containing 10 per cent. silicon and 0.2 per cent. magnesium in the modified and heat-treated condition was found to be around 9000 lb. per sq. in.   All of these values were determined on specimens cast in green sand.

Thermal Expansivity.—Silicon decreases the expansivity of aluminum. Values for several typical materials are given in Table 16.   No measure-

TABLE 16.—*Thermal Expansivity of Aluminum*

Material	Mean Coefficient Per Degree Fahrenheit		
	68° to 212° F.	68° to 392° F.	68° to 572° F.
High purity aluminum sheet...............	0.0000132	0.0000137	0.0000143
No. 12 alloy..............................	0.0000134	0.0000143	0.0000153
No. 43 alloy..............................	0.0000122	0.0000128	0.0000132
No. 45 alloy..............................	0.0000117	0.0000122	0.0000127
No. 47 alloy..............................	0.0000110	0.0000112	0.0000118

ments have been made on the alloys described in this paper, but it may be considered that the coefficient of expansion will not be materially affected by the small amounts of magnesium, copper or iron present, and that the values will be substantially the same as those of binary aluminum-silicon alloys of the same silicon content, as given in Table 16.

Elastic Modulus.—The addition of silicon to aluminum results in a fairly uniform increase of Young's modulus from about 10,200,000 lb. per sq. in. for 5 per cent. silicon to about 11,100,000 lb. per sq. in. for an alloy containing 13 per cent. silicon.[8]

DISCUSSION OF RESULTS

Although many of the alloy compositions described in this paper have useful properties in the as-cast condition, it was the particular object of this investigation to find alloys suitable for the production of heat-treated castings capable of withstanding severe service.   In 1921, heat-treated aluminum-alloy castings containing 4 per cent. copper were introduced commercially.[9]   The production of these castings has attained considerable volume and in many fields of application the product has shown ability to withstand the type of service generally described as "severe."   These castings are now manufactured to specifi-

[8] According to work by D. A. Paul in the Research Laboratories of the Aluminum Co. of America.

[9] Z. Jeffries and R. S. Archer: U. S. Patent 1572487, issued Feb. 9, 1926.

R. S. Archer and Z. Jeffries: Aluminum Castings of High Strength. *Proc.* Inst. Metals Div., A. I. M. E. (1927) 35.

cations requiring a minimum tensile strength of 29,000 lb. per sq. in. with a minimum elongation of 6 per cent., in the naturally aged condition, while higher strength with less elongation is produced by precipitation heat treatment.   Tensile properties do not, of course, completely describe the fitness of a material for all kinds of service but at least they furnish a good indication.   It is interesting, therefore, to note that strength and elongation similar to those of the commercial heat-treated 4 per cent. copper alloy castings have been obtained, on a laboratory scale, with some of the aluminum-silicon-magnesium alloys described.   Values that can be maintained in commercial production remain to be determined, but it seems that properties close to those mentioned can be obtained in such production.

Assuming that the mechanical properties of the heat-treated aluminum-silicon-magnesium alloy castings are similar to those of the heat-treated 4 per cent. copper alloy, it is of further interest to compare the other characteristics of the materials.   The machinability of the aluminum-copper alloy is somewhat better than that of the aluminum-silicon-magnesium alloys.   The latter, however, can be commercially machined with standard tool set-ups, and with adaptation of tools and machining methods to suit the material can perhaps be machined as well as the aluminum-copper alloy.

Perhaps the chief advantage of the aluminum-silicon-magnesium alloys lies in superior foundry characteristics, including ease of casting and relative insensitivity to high pouring temperature.   Corrosion resistance is higher than that of the 4 per cent. copper alloy, especially when the iron content is kept low and no precipitation heat treatment is used.   Specific gravity and thermal expansivity are lower than in the aluminum-copper alloys.   Electrical and thermal conductivity are high in the aluminum-silicon-magnesium alloys, and although reduced somewhat by the small additions of copper, are probably still higher than in most commercial aluminum alloys.

The points brought out above indicate in a general way the types of application for which the alloys described here seem especially suitable.

Modulus of Elasticity of Aluminum Alloys

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The modulus of elasticity is defined as the ratio of stress within the proportional limit to corresponding strain. This property, as thus defined, is a constant for each kind of material; and in tension or compression is usually designated by the symbol E. The modulus of elasticity serves as an index of the stiffness of a material or a measure of its ability to resist change of shape under stresses not higher than the proportional limit.

In view of the frequency with which the modulus of elasticity is used in engineering calculations, it is surprising to note the uncertainty that exists as to authentic values, and the marked lack of published information relating to the variation of the constant E within individual alloy systems. A value of 10,000,000 lb. per sq. in. has been quoted as representative of aluminum and its alloys. This value has been found to be approximately correct for pure aluminum and aluminum alloys in which the total percentage of the alloying elements is low, but seriously in error in the case of alloys that contain relatively large amounts of the alloying elements.

TABLE 1.—*Modulus of Elasticity (E) Values for Various Metals*

Metal	Modulus of Elasticity, Lb. per Sq. In.	Relative Density, Grams per Cu. Cm.[e]
Lead	2,560,000[a]	4.10
Tin	5,900,000[a]	2.70
Magnesium	6,250,000[b]	0.64
Aluminum	10,000,000[b]	1.00
Zinc	12,000,000[e]	2.60
Copper	16,000,000[a]	3.20
Iron	25,000,000[e]	2.90
Nickel	30,000,000[d]	3.20

[a] National Metals Handbook.
[b] Aluminum Co. of America.
[c] Smithsonian Physical Tables.
[d] International Critical Tables.
[e] Based on density of aluminum (2.70).

* Aluminum Co. of America.
† Aluminum Co. of America.

The purpose of this paper is to define the modulus of elasticity (E) of aluminum as affected by the alloying elements commonly used. The data presented include the results of tensile tests made on an aluminum-magnesium series of alloys, both heat-treated and not heat-treated, on a number of alloys of the aluminum-magnesium type containing different percentages of various alloying elements and on a number of aluminum alloys containing appreciable amounts of the alloying elements. The results given are qualified by a brief description of the apparatus used and of the method of determining E from the tensile stress-strain data.

APPARATUS

An Olsen 10,000-lb. capacity four-screw testing machine was used for applying loads and a Martens mirror extensometer for measuring deformations (Fig. 1). The latter instrument was selected because of its
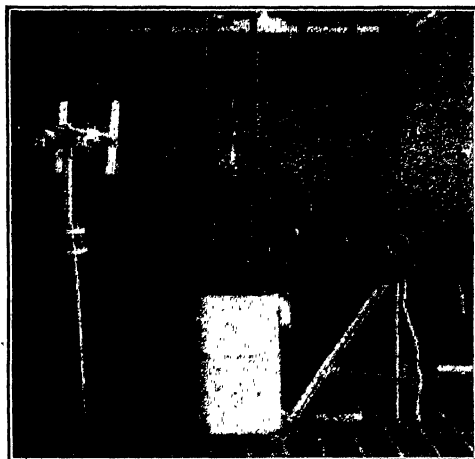
FIG. 1.—APPARATUS FOR DETERMINING TENSILE STRESS-STRAIN DATA.

sensitivity, together with its accuracy when certain precautions are observed. If the testing conditions are controlled and kept constant, the use of this instrument makes possible the detection of very small changes of modulus such as may be caused by variation of composition or fabricating procedure. Over a 4-in. gage length the Martens extenso-meter measures deformations to 0.000005 in. per in. When the testing machine and extensometer are properly used it is doubtful whether the maximum error of either exceeds plus or minus 1 per cent.

DETERMINATION OF MODULUS OF ELASTICITY FROM STRESS-STRAIN DATA

Since E is the ratio of stress to strain within the proportional limit, the determination of a modulus value involves also the selection of a

proportional limit. In the tensile test there are many factors that contribute towards a general nonuniformity of results, which make an accurate determination of these properties difficult. A discussion of these factors and their effects has been presented elsewhere.[1]

TABLE 2.—*Stress-strain Data for Curves in Fig.* 2

Stress, Lb. per Sq. In.	Strain, In. per In.	$\frac{Stress}{10,000,000}$, In. per In.	Strain $- \frac{Stress}{10,000,000}$, In. per In.
0	0	0	0
1,000	0.000105	0.000100	+0.000005
3,000	0.000305	0.000300	+0.000005
5,000	0.000518	0.000500	+0.000018
7,000	0.000710	0.000700	+0.000010
9,000	0.000903	0.000900	+0.000003
11,000	0.001100	0.001100	0.000000
13,000	0.001293	0.001300	−0.000007
15,000	0.001485	0.001500	−0.000015
17,000	0.001680	0.001700	−0.000020
19,000	0.001875	0.001900	−0.000025
20,000	0.001975	0.002000	−0.000025
21,000	0.002073	0.002100	−0.000028
22,000	0.002188	0.002200	−0.000012
23,000	0.002298	0.002300	−0.000002
24,000	0.002420	0.002400	+0.000020
25,000	0.002565	0.002500	+0.000065
26,000	0.002723	0.002600	+0.000123
27,000	0.002950	0.002700	+0.000250
28,000	0.003268	0.002800	+0.000468
29,000	0.003733	0.002900	+0.000833
30,000	0.004238	0.003000	+0.001238
31,000	0.004843	0.003100	+0.001743
32,000	0.005888	0.003200	+0.002688

The proportional limit of a metal is determined by measuring increments of strain resulting from constant increments of stress, and then determining the highest stress at which there is no increase in the strain increment. This suggests the following methods of calculating E from stress-strain data: (1) By dividing the stress at the proportional limit by the corresponding strain; (2) by dividing the average of the stress increments within the proportional limit by the average of the strain increments; and (3) by drawing a straight line through the plot of the stress-strain data and then determining E from the slope of this line. Experience with all of these methods has demonstrated that the error in modulus value occasioned by their use may easily be as much as 3 or 4 per cent., if not greater.

[1] R. L. Templin: The Determination and Significance of the Proportional Limit in the Testing of Metals. *Proc. Amer. Soc. Test. Mat.* (1929) 29, Pt. 2.

The method of determining E in the present investigation has been described by Dr. L. B. Tuckerman.[2] Instead of plotting the ordinary stress-strain diagram, differences between observed strains and computed strains are plotted as abscissas to a magnified scale with stresses as ordinates. The points within the straight-line portion of the curve are then averaged by a straight line, and the correct modulus determined by using the slope of this straight line as the correction on the trial modulus. A typical set of such data is shown in Table 2 and the corresponding curves in Fig. 2.

The personal equation factor enters into the above procedure only in the drawing of the straight line as an average of the several points. With satisfactory data and the use of proper scales, however, the slope of the line cannot be varied enough to cause more than 0.2 or 0.3 per cent. change of modulus. This method offers about the only means for the detection and elimination of bad readings such as the first few plotted in the region of zero stress (Fig. 2).

DISCUSSION OF RESULTS

Values determined according to the methods outlined show that the modulus of elasticity can be increased by the addition to aluminum of such metals as copper, nickel, silicon, iron or manganese, and decreased by the addition of magnesium.

Fig. 3 shows the variation of E for heat-treated aluminum-magnesium alloys containing from 6 to 18 per cent. magnesium, and for alloys not heat-treated containing from 6 to 14 per cent. magnesium. Both curves tend to substantiate the following statement; namely, that magnesium held in solid solution with aluminum does not have as great an influence on the modulus of elasticity as when it is present as a free constituent.

At ordinary temperatures less than 4 per cent. of magnesium is soluble in aluminum as compared to about 12 to 14 per cent. at 450° C.[3] Interpolation of the two curves in Fig. 3 indicates that heat treatment has little effect on the modulus of elasticity until magnesium is present in amounts greater than about 6 per cent. Above this percentage the modulus of elasticity of unheat-treated aluminum-magnesium alloys decreases rapidly, and is consistently lower than that of the heat-treated alloys, where it does not begin to decrease until the magnesium content exceeds about 12 per cent. At 10 and 14 per cent. magnesium E is increased about 2.5 per cent. by heat treatment.

The data plotted in Fig. 4 show the changes of E produced by the addition of various alloying elements to the aluminum-magnesium type

[2] L. B. Tuckerman: Discussion of the paper by R. L. Templin on The Determination and Significance of the Proportional Limit in the Testing of Materials. *Idem.*

[3] E. H. Dix, Jr. and F. Keller: Equilibrium Relations in Aluminum-magnesium Alloys of High Purity. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 351.

of alloy.   While the problem is complicated somewhat by the presence of two alloying elements, the data are presented because they show clearly the effects of the addition of the various metals to aluminum. The magnesium content in every case was constant at 10 per cent.
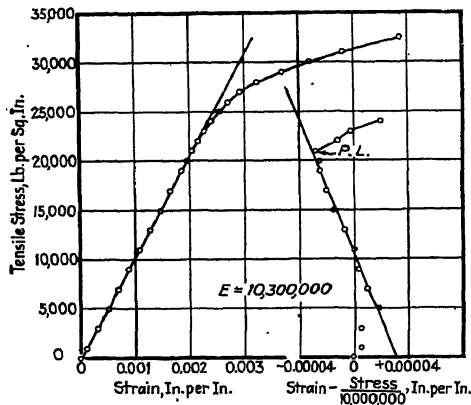
FIG. 2.—ORDINARY STRESS-STRAIN CURVE AND METHOD OF PLOTTING DIFFERENCES BETWEEN OBSERVED AND COMPUTED STRAINS.
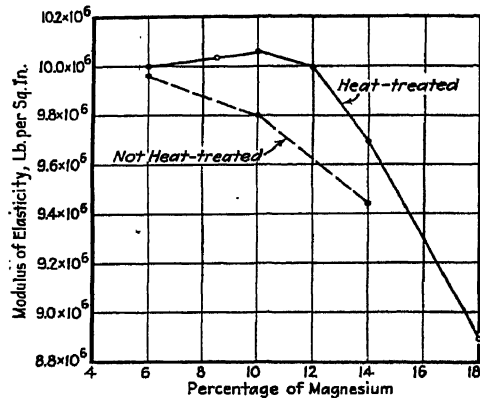
FIG. 3.—CHANGE OF MODULUS PRODUCED BY ADDITION OF MAGNESIUM TO ALUMINUM.
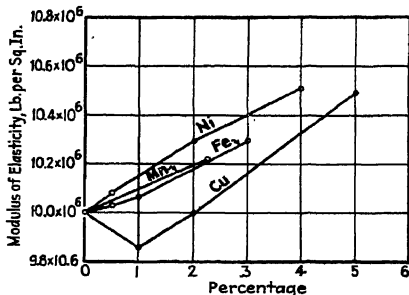
FIG. 4.—CHANGE OF MODULUS PRODUCED BY ADDITION OF ALLOYING ELEMENTS TO ALLOY OF ALUMINUM-MAGNESIUM TYPE.
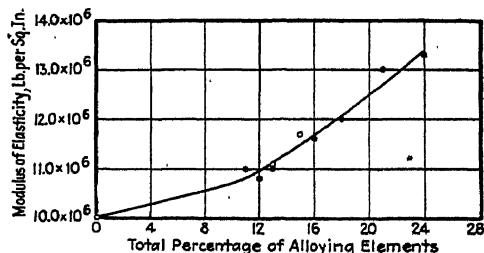
FIG. 5.—CHANGE OF MODULUS PRODUCED BY ADDITION OF LARGE AMOUNTS OF COPPER, NICKEL AND SILICON TO ALUMINUM.

Nickel, iron, copper or manganese produce fairly uniform increases of E, as the percentage of each is increased.   Apparently, nickel has the greatest effect and copper the least, with manganese and iron intermediate between the two.   A modulus of elasticity value for pure manganese is not available, but it is interesting to notice that the other metals produce changes somewhat in the order of their respective modulus values.   Taking as an example the changes produced at an alloying content of 3 per cent.: Nickel, with E equal to 30,000,000 lb. per sq. in., produces an increase of about 4 per cent.; iron, with E equal to approxi- ·

mately 25,000,000 lb. per sq. in., causes an increase of almost 3 per cent.; while copper, with E approximately 16,000,000 lb. per sq. in., causes an increase of about 1.5 per cent.

Results of tensile stress-strain tests of aluminum casting alloys show the pronounced increases of modulus of elasticity that may be caused by the addition to aluminum of appreciable amounts of these metals and silicon, to form binary, ternary or quaternary alloys (Table 3).

Probably the most significant values in Table 3 are those given for alloys A and B, which have silicon as their predominating alloying element. In the former alloy, E is increased about 10 per cent. by the presence of 13 per cent. silicon, and, in the latter alloy about 20 per cent. by the presence of 14 per cent. silicon and relatively small amounts of copper, nickel and magnesium. It is important to note that the density of silicon, and therefore of the above alloys, is somewhat less than that of aluminum. Hence, in B alloy the modulus of elasticity has been increased about 20 per cent. without any increase in density.

TABLE 3.—*Modulus of Elasticity Values for Some Cast Aluminum Alloys*

Alloy	Modulus of Elasticity (E), Lb. per Sq. In.
A (13% Si)	11,100,000
B (14% Si, 1.15% Cu, 2.5% Ni, 1% Mg)	12,000,000
C (10% Cu, 1.25% Fe, 0.25% Mg)	10,800,000
D (12% Cu)	10,800,000
E (12% Cu, 0.75% Mn)	11,000,000
F (5% Cu, 6% Si)	11,000,000
G (8% Si, 4% Cu, 4% Ni)	11,600,000
H (10% Cu, 4% Ni, 1% Mn)	11,700,000
I (7% Si, 7% Cu, 7% Ni)	13,000,000
J (10% Si, 10% Cu, 4% Ni)	13,300,000

Fig. 5 represents the plot of the values of E listed in Table 3 against the total percentage of the alloying elements present in each alloy. It is apparent that this curve rises uniformly and that no serious discrepancies exist between the curve and the plotted data. Although there is some doubt as to the exact shape of the lower portion of this curve, it is evident that E increases more rapidly above an alloying content of 12 per cent. than below. At this percentage, the modulus of elasticity has been increased approximately 1,000,000 lb. per sq. in., while at 24 per cent. the increase is about 3,000,000 lb. per sq. in. The "knee" in the curve at 12 per cent. may be attributed to the presence of nickel at higher percentages. An approximate modulus value for an alloy of known composition can probably be selected from this curve, bearing in mind the composition of the alloys from which the curve is plotted.

CONCLUSIONS

When the number of alloy systems to be investigated is considered together with the effects of different variables within each of these systems, the magnitude of the modulus problem is evident. The present investigation is of a preliminary nature but the authors believe that the results contained in this paper are valuable because they furnish a general idea of the variation of E produced by the addition of the more common alloying elements to aluminum. The following conclusions seem predominant:

1. A general increase of modulus of elasticity results with the addition of iron, silicon, copper, nickel or manganese to aluminum.

2. In certain of the commercial aluminum alloys the modulus of elasticity is increased as much as 20 to 30 per cent. by the presence of considerable amounts of the metals mentioned above.

3. The results obtained indicate that copper, iron and nickel produce changes somewhat in the order of their respective modulus values, nickel having the greatest effect and copper the least.

4. The addition of silicon to aluminum results in an increase of modulus without any increase in the density of the metal.

5. In heat-treated aluminum-magnesium alloys the modulus of elasticity does not decrease until magnesium is present in amounts greater than about 12 per cent.; in alloys that have not been heat-treated the decrease occurs in the region between 6 and 10 per cent. magnesium.

6. It may be concluded from paragraph 5 that magnesium held in solid solution in aluminum does not have as great an influence on the modulus of elasticity as when it is present as a free constituent.

Quenching of Alclad Sheet in Oil

By Horace C. Knerr,* Philadelphia, Pa.

(Chicago Meeting, September, 1930)

It has been shown[1] that the resistance to corrosion of duralumin sheet is greatly influenced by the quenching medium used in heat treatment, or, more specifically, by the rate of cooling during quenching. The severity of corrosive attack after exposure to salt-water spray increases in the following order:

Quenching Medium	Degree of Corrosion, by Inspection, After 30 Days of Salt-water Spray Test
Water, cold (60° F.)	Very slight.
Water boiling	Slight, but more than with cold water.
Oil (70° F.)	Slight, but more than with cold water.
Air, fan blast, 65° F.	Severe, scaled.
Air, still, 65° F.	Deeply scaled.

The tensile strength, yield point and elongation are only slightly affected by the quenching medium, as shown in Table 1.

TABLE 1.—*Influence of Quenching Medium on Tensile Properties of Duralumin (not corroded)*[a]

Quenching Medium	Yield Point,[b] Lb. per Sq. In.	Ultimate Strength,[b] Lb. per Sq. In.	Elongation,[b] Per Cent. in 2 In.	Elongation,[b] Per Cent. in 4 In.
Specimen ⅙ in. thick				
Cold water 60° F.	36,560	61,640	18.9	16.6
Boiling water	35,640	61,500	19.1	17.6
Oil (Houghton's)	35,300	61,400	18.9	17.3
Air blast	35,560	59,330	18.0	15.4
Still air	33,000	58,900	18.3	16.0
Specimens ⅛ in. thick				
Cold water	38,700	61,000	19.2	16.9
Boiling water	35,900	61,740	19.8	17.2
Oil (Houghton's)	38,300	61,700	19.8	15.7
Air blast	34,250	58,580	17.5	16.0
Still air	36,200	58,050	18.0	15.0

[a] H. C. Knerr: *Op. cit.*
[b] Tensile test requirements: yield stress, 25,000 lb. per sq. in. minimum; ultimate stress, 55,000 lb. per sq. in. minimum; elongation in 2 in., 18 per cent. minimum.

* Consulting Metallurgical Engineer. President, Metallurgical Laboratories, Inc.
[1] H. C. Knerr: Duralumin. *Trans.* Amer. Soc. Steel Treat. (1922) **3**, 13.

It has been customary to specify that duralumin be quenched in cold water when the parts are to be exposed to the action of moisture, as in naval aircraft.   Duralumin parts frequently are heated in a molten bath of sodium nitrate, prior to quenching.   Water readily dissolves any adhering salts whereas oil does not.   It is impracticable to heat large parts or those of bulky and irregular shape in a molten salt bath because of the severe distortion which occurs when the work is lowered into and raised from the bath.   Salt baths also have limitations, for other reasons. Therefore much duralumin is heat-treated in electric furnaces of the oven type.

Duralumin is soft immediately after quenching, and it is possible therefore to rework it sufficiently, after heat treatment, to remove moderate distortion that may have occurred.   When large or bulky parts are quenched in cold water, distortion due to quenching strains may be severe, and a large amount of labor may be required to rectify this.

Quenching in oil, such as is ordinarily used in the heat treatment of steel aircraft parts, results in much less deformation than quenching in water.   Moreover, electric furnaces that are used for heat-treating steel parts may be used for the treatment of duralumin, provided temperature regulation and uniformity are satisfactory.   Such furnaces usually are provided with tanks for quenching in oil, as oil is considered the preferable medium for quenching steel aircraft parts.   Therefore it would be highly advantageous, both from the standpoint of available equipment and of minimizing distortion and thereby reducing working costs, to quench duralumin parts in oil.   The moderately increased susceptibility to corrosion following oil quenching as compared with cold-water quenching has hitherto been an argument against this practice.

Alclad sheet has been developed since the date of the discovery of the variation in corrosion following various quenching treatments. Alclad sheet consists of ordinary duralumin carrying on its two surfaces a thin layer of aluminum of high purity.   The aluminum is alloyed with and firmly attached to the duralumin.   It has a relatively high resistance to corrosion, and therefore acts as a protective coating for the duralumin. Heat-treating practice ordinarily is the same as for duralumin, and the physical properties are also the same, except for the slight effect of the pure aluminum surface, which lowers the tensile strength figured on the total cross-sectional area by a few per cent.   Alclad sheet is now employed extensively in preference to ordinary duralumin where resistance to corrosion is important, as in the hulls of flying boats, in pontoons, in the surfaces of fuselages and so forth.   Such parts are bulky and heat treatment in an oven electric furnace is ordinarily preferable.   In order to reduce the distortion during quenching to a minimum, it would be very desirable to quench these parts in ordinary quenching oil.

As the resistance to corrosion of Alclad sheet depends upon the surface layer of aluminum, and not upon the character of the internal duralumin, it is to be expected that no such difference in resistance to corrosion after treatment in various quenching mediums would be experienced as is characteristic of duralumin. Tests have been carried out for the purpose of obtaining information on this point.

TABLE 2.—*Comparison of Alclad Sheet and Duralumin Quenched in Various Mediums and Exposed to Corrosion 400 Hours*

Properties	Quenching Mediums								
	Water, 60° F.		Oil, 60° F.		Oil, 140° F.		Still Air, 66° F.		Water, Boiling
Duralumin	Spec. 1	Spec. 2	Spec. 3	Spec. 4	Spec. 5	Spec. 6	Spec. 7	Spec. 8	Spec. 9
Tensile strength, lb. per sq. in..........	62,500	61,500	56,900	58,000	59,800	60,000	49,400	51,000	60,500
Elongation, per cent. in 2 in............	16.5	18.5	10.5	11	16	15.5	8	9.5	17
Alclad Sheet	Spec. 11	Spec. 12	Spec. 13	Spec. 14	Spec. 15	Spec. 16	Spec. 17	Spec. 18	Spec. 19
Tensile strength, lb. per sq. in..........	59,200	57,500	58,000	58,900	57,500	56,400	55,000	54,100	55,800
Elongation, per cent. in 2 in............	19.5	18.5	19.5	20	20	21.5	17.5	17.5	19

METHOD OF TEST

A series of standard tensile test specimens having a gage section $\frac{1}{2}$ in. wide and 2 in. long were cut from an Alclad sheet and from a duralumin sheet, both $\frac{1}{16}$ in. thick. All were heated to 930° F. in an electric muffle furnace, held for 20 min. and quenched in various mediums, as indicated in Table 2. After aging, these specimens were exposed to corrosion by the alternate immersion method in a 20 per cent. solution of salt water containing 10 per cent. hydrogen peroxide by volume, as described by H. S. Rawdon,[2] of the U. S. Bureau of Standards, who reports that corrosive effects equivalent to those produced by the salt-water spray method can be obtained in relatively short time. The specimens are immersed in the solution for 1 min. and then raised and allowed to dry in air for 14 min., etc. The peroxide is renewed twice a week. Corrosion was continued until bend tests made on the butt ends of duralumin specimens showed pronounced embrittlement. All the specimens were then tested in tension, using the Otey type of special grips with spherical heads. This period of corrosion, 400 hr., did not greatly affect

[2] Private communication.
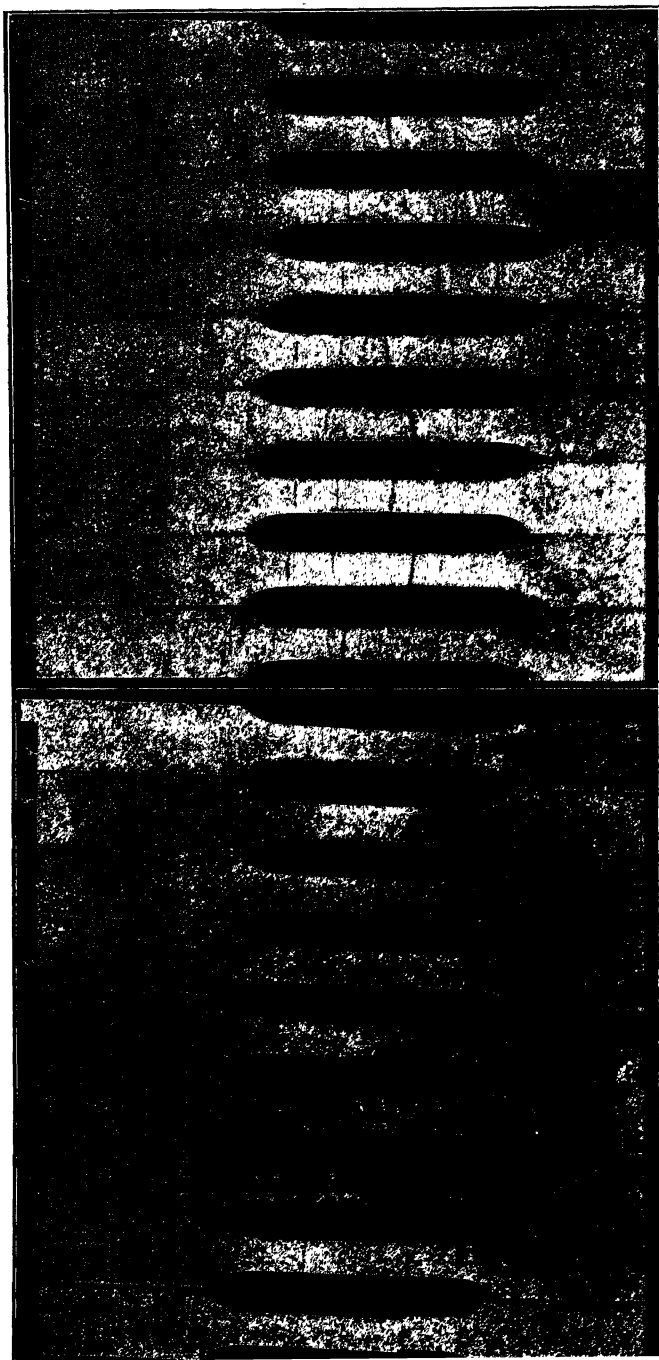
FIG. 1.—SPECIMENS 1 TO 9, DURALUMIN AFTER TEST; SPECIMENS 11 TO 19, ALCLAD SHEET AFTER TEST.

the tensile strength of any of the specimens but did show a pronounced influence upon the elongation. The latter is regarded as an excellent comparative measure of this type of corrosion.

The percentage of elongation of the duralumin was characteristically reduced in the specimens quenched in oil[3] and in still air, but the elongation of the Alclad specimens varied little with the quenching mediums and was fully as good for oil quenching, either hot or cold, as for quenching in cold water.

Specimens of each type were tested without exposure to corrosion, having been quenched in cold water, and showed normal characteristics. Although the present tests were made with a small number of specimens under limitations as to time and expense, the results appear to be definite. Additional tests are being conducted with the cooperation of T. W. Downes, metallurgist at the Naval Aircraft Factory, using the salt-water spray method. At date of writing, it is reported that after exposure for 60 days the duralumin specimens quenched in various ways show distinct visible corrosion, while the Alclad specimens show none.

CONCLUSIONS

The resistance of Alclad sheet to corrosion is much less affected by the quenching medium than that of duralumin. It appears that Alclad sheet may be quenched in a good quenching oil, such as is used in the heat treatment of steel, without serious sacrifice either of tensile properties or corrosion resistance and with much less distortion as compared with quenching in cold water.

ACKNOWLEDGMENT

The author wishes to acknowledge the valuable assistance of Mr. M. M. Kennedy and Miss F. Bachtiger, of his staff, in conducting the investigation, and of Mr. T. W. Downes and Mr. Tripolitis of the Naval Aircraft Factory in making the tensile tests.

DISCUSSION

(H. W. Gillett presiding)

E. H. DIX, JR., New Kensington, Pa.—In considering this paper, we should bear in mind that the tests are not extensive, as Mr. Knerr has pointed out, and particularly that they are confined to one thickness of Alclad sheet. I think he has shown conclusively that under the conditions described in the paper, Alclad sheet can be safely quenched in oil, but it would be extremely dangerous to conclude from this paper that the precautions ordinarily employed in heat-treating duralumin sheet, in order to obtain maximum corrosion resistance, can be completely ignored in the case of Alclad sheet.

---

[3] For some reason, the duralumin specimens quenched in hot oil did not show great embrittlement after corrosion, and were better than those quenched in cold oil.

In our own company, when we have been asked such questions as this, we have taken the attitude that any deviation from good commercial practice on duralumin sheet should not be countenanced for Alclad sheet until the conditions under which it is proposed to treat the material have been thoroughly investigated and it has been determined that for the range of thickness to be used, the practice in question has no detrimental effect on the corrosion resistance. With the present state of our knowledge, this is the only safe conclusion in regard to this new material.

While we are on this subject of the effect of heat treatment on the corrosion resistance of duralumin alloys, I should like to add that while much has been said regarding the detrimental effects of slow quenching, by which we have ordinarily meant quenching in hot water or oil or air, there is another factor not generally appreciated, of which the influence is the same, and perhaps often more severe than the quenching medium, and that is the possibility of any delay between withdrawal from the heat-treating furnace or bath and the quenching. It is surprising how rapidly the temperature of duralumin sheet, even in rather large masses, will fall in a very short time. I firmly believe that many of the failures encountered in the corrosion of duralumin sheet thought to have been heat-treated under proper conditions may be attributed to an unobserved delay which has caused the temperature to drop to such an extent that it did not make any difference how it was quenched after that.

H. S. RAWDON, Washington, D. C.—These results of Mr. Knerr's tie in very nicely, in many respects, with the work in progress at the Bureau of Standards, but in some respects they do not fit in at all; for instance, the results given on page 489 for the properties of duralumin sheet that has been quenched in different ways and exposed to corrosion for 400 hr. Mr. Knerr has used the same method that has been used at the Bureau of Standards for this. The properties of the cold-water quenched sheet are practically the same as the properties of the hot-water quenched sheet at the end of 400 hr. We do not get anything at all like that. It is true that in the tests made at the Bureau, the tensile strength did not drop much. But we have found that the ductility of hot-water quenched material after 10 days, for example, by corrosion by this method, would be more of the order given for the air-quenched material, that is 8 per cent. instead of 17 per cent. At the beginning, material has only 17 or 18 per cent. elongation. Those results do not tie in at all with those obtained at the Bureau. I am at a loss to explain them.

As judged by the results in the upper row, one might almost say that hot-water quenching perhaps would be preferable to cold-water quenching.

The results obtained upon quenching the aluminum-coated duralumin, however, do tie in very nicely indeed with what has been found at the Bureau. It makes no difference practically whether the Alclad sheet is quenched in any medium, hot or cold water or oil, as to its subsequent behavior in the laboratory corrosion test or in the exposure in the atmosphere later. The exposure tests have been in progress somewhat over two years, and the Alclad duralumin seems to be standing up remarkably well regardless of what was done to it. The duralumin sheet itself, however, is confirming the predictions that were based upon the corrosion tests, that is, the hot-water quenched material is not standing up so well in the atmosphere as the cold-water quenched, and the oil-quenched is not standing up so well, the results for oil-quenched material being intermediate between those for the hot-water and cold-water quenched materials.

There is another matter which, while not exactly in line with the present paper, bears on the corrosion tests. The tests which have been in progress for about three and one-half years have shown that the rate of embrittlement for the hot-water quenched materials is relatively high at the beginning; the curve representing loss of ductility with time, however, flattens and becomes roughly parallel to the base line.

It now appears that if the experiments are continued for the five-year program that was initially planned, the rate of embrittlement may not be any more severe at the end of five years than it is now. However, the material that was acceleratively aged is behaving very differently, and the rate of embrittlement is much greater for this than for the hot-water quenched sheets. There is almost no elongation in the acceleratively aged duralumin after the three years, whereas the hot-water quenched material, even after severe exposure in the tropics, has not gone entirely. It may be of the order of 6 per cent. elongation or so. So it seems that the initial effect may be a surface effect. It follows then that the larger the mass, the less severe will be the effect of corrosion on the properties of the metal. On the other hand, the thinner the sheet, the more severe is that effect.

H. W. GILLETT, Columbus, Ohio.—The author has only one specimen in boiling water. Apparently the conclusions have been drawn on a single specimen. I do not see offhand why that should differ from the others, because they are apparently all done together. You renew the peroxide more often than twice a week, do you not?

H. S. RAWDON.—Yes, about three times a week.

H. W. GILLETT.—I cannot reconcile that, myself. If it were not that the tensile strength is still up, I might think that there was a mistake and that it was 7 per cent. I would look for 7 per cent. more than I would look for 17 per cent.

On the very thin Alclad, do you find that hot-water quenching is just as good as cold?

H. S. RAWDON.—We have not tried it out on the very thin sheet, only the 14-gage material has been used.

H. W. GILLETT.—Mr. Dix's comment probably was aimed at that very thin material. You would not question that in 14 gage hot water or oil quenching is all right for Alclad?

E. H. DIX, JR.—I think it is all right. These results show it to be all right, but I still feel there are other conditions that may be encountered which would not justify us in completely disregarding most of the things we have known to be necessary.

H. W. GILLETT.—Of course, if we are satisfied that the corrosion resistance is not impaired, obviously the thing to do is to use the quenching method that will give less distortion and more latitude in methods of heat treatment that can be applied.

E. H. DIX, JR.—I would desire to check any given heat-treatment procedure.

INDEX

(NOTE: In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the titles of papers in *italics*.)